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Sulphur isotope geochemistry

H. G. THODE,* J. MONSTER and H. B. DUNFORD

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Abstract—Sulphur isotope abundances of thirty-nine specimens of seventeen meteorites are reported. The results show again the remarkable constancy of the sulphur isotope ratios for meteorites of all types. However, differences in the S^{32}/S^{34} ratios of 0·4 ‰ would appear to be significant. The S^{32}/S^{34} ratio for meteorites is discussed as a possible base level from which fractionation in the earth's crust began. The value is compared with estimates of average values found for terrestrial samples including some recent results of igneous intrusives.

A large suite of sea water samples collected from widely separated points in three oceans at various depths have also been investigated and the S^{32}/S^{34} ratios reported. The results show that the sulphate in the three oceans is exceedingly uniform in isotope ratio, with an enrichment of 20·1 ‰ ± 0·3 in S^{34} over that of the meteoritic standard. Sulphur isotope ratios of sulphur in a sea shell, sulphides in shallow ocean sediments, sulphate in rain water and in present-day formation of gypsum evaporites from the sea, have been measured and are compared to the sea water level. The geochemical sulphate cycle is discussed in the light of these results.

INTRODUCTION

IT IS well established from theory and experiment that the isotopes of sulphur differ markedly in their chemical properties and are fractionated in chemical processes both in the laboratory and in nature. The principles of isotope fractionation are now fairly well understood, and isotope fractionation factors for certain isotopic reactions can be predicted from theory. The measurement of the variations in isotope ratios that occur in natural samples provides, therefore, considerable information concerning the origin, mode of formation of certain rocks and minerals, and make it possible to trace out processes which occurred millions of years ago. Studies of the sulphur isotope distribution in natural samples have been particularly interesting and have led to the solution of a number of important geochemical problems.

However, the interpretation of isotope distribution data in terms of natural processes and earth history is often difficult, firstly because of the complexity of natural processes, and secondly because of the lack of base levels of isotope ratio from which isotope fractionation may be reckoned. In this latter connexion, meteoric sulphur provides perhaps the most important base level from which sulphur isotope fractionation has occurred.

Meteorites

Early work by MACNAMARA and THODE (1950) showed that whereas the S^{32}/S^{34} ratio for terrestrial samples varied by as much as 10 per cent, this ratio for meteoritic sulphur was remarkably constant. Furthermore, this constant value was found to coincide approximately with the median ratio found for terrestrial sulphur and to fall in the range of isotope ratios found for rocks presumably of igneous origin. These results led MACNAMARA and THODE (1950) to suggest that the sulphur isotope ratio found for meteoritic sulphur is the primordial value and that in the earth's

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crust, fractionation of the sulphur isotopes has occurred, thereby spreading out the isotope ratios above and below the primordial or base level.

Regardless of the validity of this suggestion, meteoritic sulphur provides an ideal standard of comparison for all isotope fractionation studies because of the remarkable constancy of the isotope ratio for meteorites of all types. The sulphur isotope ratio for any given sample of sulphur is therefore expressed relative to the sulphur isotope ratio for meteorites as a δ-value, defined as follows:

$$\delta S^{34}\,‰ = \frac{(S^{34}/S^{32})\text{sample} - (S^{34}/S^{32})\text{meteoritic sulphur}}{(S^{34}/S^{32})\text{meteoritic sulphur}} \times 1000 \qquad (1)$$

It should be pointed out that certain workers in the field have defined $\delta S^{34}\,‰$ in terms of the reciprocals of the isotope ratios used above. The two formulae give slightly different δ-values, the difference amounting to 0·4 ‰ for a δ-value of +20 ‰. Unfortunately some authors have defined δS^{34} as above but appear to have used the other formula in their calculations. In quoting the work of others we have recalculated the δ-values in terms of the above definition using their published S^{32}/S^{34} ratios.

Small variations in the S^{32}/S^{34} ratios relative to a standard as expressed by $\delta S^{34}\,‰$ above may be measured with a modern isotope ratio mass spectrometer with a precision of better than 0·02 per cent. Since meteoritic sulphur is now used exclusively as a standard of comparison, δ-values for a given sample obtained in different laboratories are comparable. However, the actual S^{32}/S^{34} ratio quoted for a sample will depend on the S^{32}/S^{34} ratio assigned to meteoritic sulphur. Since absolute ratios of the sulphur isotopes are not known to better than 1 per cent and various values have been assigned to the S^{32}/S^{34} ratio for meteorites (from 22·20 to 22·225) it is important that all isotope ratios be expressed relative to the meteoritic standard as $\delta S^{34}\,‰$ defined above.

In the calculation of δS^{34}, the absolute ratio assigned to meteoritic sulphur comes only in the denominator of equation (1) since the method of measurement involves the comparison of the sample and the meteoritic standard directly. This means that a 0·1 per cent variation in the S^{32}/S^{34} ratio arbitrarily assigned to the meteoritic standard by the different workers will only effect the calculated δS^{34} value by the same percentage, which is not significant.

In their original work on the distribution of the sulphur isotopes in nature, Thode, Macnamara and Collins, used Park City, Utah, pyrite as a standard and assigned it an S^{32}/S^{34} ratio of 22·120. On this basis, six meteorites were found to have an average S^{32}/S^{34} ratio of 22·22, the values varying from 22·20 to 22·24 (Macnamara and Thode, 1950). Since then meteoritic sulphur has been used as a standard and various S^{32}/S^{34} ratios have been assigned to it, ranging from 22·20 to 22·225. The latter value which represents a more recent comparison of meteoritic sulphur with Park City Pyrite is now used in this laboratory.

Two questions arise: (1) how constant are the sulphur isotope ratios for meteoritic sulphur; and (2) do meteorites give the primordial value? Trofimov (1949) examined four meteorites and reported a maximum spread of 0·6 per cent in the S^{32}/S^{34} ratio. Later, Macnamara and Thode (1950) examined six different meteorites, and in one case, four different specimens of one large meteorite, and

reported a maximum spread of 0·15 per cent in the S^{32}/S^{34} ratio. Finally, VINOGRADOV (1958) indicated identical sulphur isotope ratios for some eleven stone meteorites found in the U.S.S.R. giving an S^{32}/S^{34} value of 22·20 for each meteorite. During the past 6 years a careful study has been made of the sulphur isotope ratio in meteorites using an isotope ratio mass spectrometer of high sensitivity. This instrument makes possible the measurement of small differences in S^{32}/S^{34} ratios with a precision of $\pm 0{\cdot}01$ per cent. Altogether, thirty-nine specimens of seventeen different meteorites have been investigated, including eight siderites, six stones and one carbonaceous meteorite. A very careful comparison of several pairs of samples was carried out in order to establish limits on the variations that occur. The results of these investigations are reported below. The average value of the S^{32}/S^{34} ratio for the earth is discussed in light of recent sulphur isotope measurements made on rocks of massive igneous intrusions and on materials from volcanoes and fumaroles.

Sea water

Also of considerable importance in the interpretation of sulphur isotope distribution data in natural samples is the sulphur isotope ratio for sea water sulphate. Sea water sulphate enters into many of the large scale oxidation reduction processes which take place in the sea and in the muds at the bottom of the sea and is the source of many large sulphate and sulphide deposits. The sulphur isotope ratio for sea water sulphate therefore provides a base level from which isotope fractionation may be reckoned. For example, THODE *et al.* (1951), JONES *et al.* (1956), JONES and STARKEY (1957), HARRISON and THODE (1958b) have shown that fractionation of the sulphur isotopes occurs in the bacterial reduction of sulphate which process takes place on a large scale in the shallow muds at the bottom of the sea. Also, sea water sulphate was probably the original source of sulphur now found in petroleum deposits of marine origin. In all processes where sea water sulphate is reduced, isotope fractionation may occur and the extent of this fractionation may be determined by comparing the S^{32}/S^{34} ratio of the reduced sulphide with that of sea water sulphate. The sea, in effect, provides an infinite reservoir of sulphur with a fixed S^{32}/S^{34} ratio.

Here the important questions are: How uniform is the S^{32}/S^{34} ratio in the sea? What is the present value relative to meteoritic sulphur or the primordial sulphur? How has this value been changing in time?

TROFIMOV (1949) found that sea water sulphate was enriched in S^{34} as compared to other sources. THODE *et al.* (1949), had previously found that evaporites from the sea, gypsum and anhydrite, were highly enriched in S^{34} and later, SZABO *et al.* (1950), confirmed the high enrichment of sea water sulphate in the heavy sulphur isotope S^{34}. Four samples taken from the Atlantic, Arctic and Pacific oceans were found to have an average enrichment of 21·4 p.p.m. with respect to meteoritic sulphur (δ ‰ $S^{34} = +21{\cdot}4$) the values ranging from +19·1 to +23·8. Since then, many sea water sulphate samples have been investigated by VINOGRADOV *et al.* (1956a), SAKAI (1957), FEELY and KULP (1957), AULT and KULP (1959). Of these investigators, AULT and KULP carried out the most extensive investigation and have reported results for some twenty-five different samples taken from nine

different locations and at different depths. Their sea water δ-values range from +19·3 to +21·1.

Over the past 7 years, some forty different sea water samples collected from sixteen different locations and at various depths have been investigated in this laboratory. Particular attention was paid to the method of sample preparation in an effort to determine an absolute δ-value for the samples as well as to determine the extent of isotope ratio variation. Sulphate in recent evaporites, in fresh water lakes and in the sea at the mouths of rivers have also been studied and their isotope ratios compared.

Experimental

Preparation of samples

All samples of sulphur are analysed in the mass spectrometer as SO_2. Sample preparation procedures were developed to produce SO_2 free of any impurity and in good yield so as to avoid appreciable sulphur isotope fractionation. In this connexion, yields of over 99 per cent were obtained in all processes with the exception of the final burning of Ag_2S in the high-temperature furnace in which case yields of only 90 per cent were obtained. In the case of sea water, the procedure involved: (1) the precipitation of sulphate as $BaSO_4$; (2) reduction to hydrogen sulphide; (3) conversion to metal sulphide (Ag_2S); and finally, (4) conversion to SO_2 by burning in a stream of pure O_2. In the case of meteorites, two methods were used: (1) the direct burning of the troilite (FeS) to SO_2 in a stream of oxygen; (2) the treatment of meteorite sulphides with HCl and the conversion of the hydrogen sulphide produced to Ag_2S and finally to SO_2 by the burning procedure. Many of the meteorites studied contained showings of troilite (FeS). In these cases, the troilite was removed for analysis. However, in the case of the stones, the samples were completely pulverized and burned in a stream of oxygen after roasting in an inert atmosphere at 450°C.

Reduction of barium sulphate

The $BaSO_4$ samples are reduced to H_2S by a boiling mixture of HI, H_3PO_2 and HCl. This method is a modification of the micro-method for sulphur described by Pepkowitz and Shirley (1951). The composition of the reducing mixture used is: 500 ml (= 850 g) HI, (d = 1·7); 816 ml concentrated HCl; 245 ml H_3PO_2 (50 per cent). When preparing this mixture, care is taken to remove any sulphur compounds present by simply boiling the mixture for 45 min. This will expel any sulphur present as H_2S. The reduction is carried out in a 200-ml flask provided with a reflux condenser. The H_2S swept out with a stream of nitrogen is washed with distilled water and finally absorbed in a solution containing cadmium acetate, acetic acid and distilled water. Because silver sulphide is easier to filter than cadmium sulphide, the latter is converted to Ag_2S by adding 0·1 N $AgNO_3$. After coagulation on heating, the Ag_2S is filtered through glass wool and washed twice with concentrated NH_4OH. The Ag_2S is then dried in an oven at 120°C.

Burning procedure

The sulphide samples are placed in a quartz boat and burned in a stream of

oxygen inside a fused quartz tube at a temperature of 1350°C, the temperature of the tube being maintained by an electric furnace. The oxygen used is purified by passage through Ascarite (NaOH), Anhydrone ($MgClO_4$) and concentrated sulphuric acid. Hydrocarbons can be eliminated by passing the oxygen through a zircon tube at 1350°C. The SO_2 produced is sealed in a Pyrex tube for mass spectrometric analysis after the removal of excess oxygen, water and carbon dioxide.

In the burning procedure, there is always some SO_3 produced according to the reaction:

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3 \qquad (2)$$

However, the yield of SO_3 decreases rapidly with temperature and is less than 5 per cent at 1200°C. Any appreciable production of SO_3 in the preparation of SO_2 would result in a high S^{32}/S^{34} ratio for a sample, since S^{34} is favoured in the SO_3. The exchange constant for the reaction:

$$S^{34}O_2 + S^{32}O_3 \rightleftharpoons S^{32}O_2 + S^{34}O_3 \qquad (3)$$

is calculated to be 1·037, 1·003 and 1·001, at 25°, 900° and 1500°, respectively. A consideration of both reactions (2) and (3) indicates that isotope fractionation effects will be negligible if samples are burned above 1350°C. Also, since only differences in isotope ratios are involved, small isotope fractionation effects in sample preparations will cancel providing the sample and standard are prepared in an identical manner (burned at the same temperature).

It is found, however, that considerable isotope fractionation occurs when SO_2 samples are burned at low temperatures in a simple combustion tube heated by gas burners due to SO_3 production. In particular, sulphides mixed with inactive ore burn at low temperatures and very poor yields of SO_2 are obtained. These samples are of little use for isotopic analysis. In the case of Ag_2S samples, much higher temperatures are attained in the simple combustion tube burning procedures as evidenced by the appearance of molten Ag(melting at 900°C). However, even in this case appreciable quantities of SO_3 are formed.

Results and Discussion

Meteorites

Table 1 gives the S^{32}/S^{34} ratios and δ-values relative to the mean for sulphur found in seventeen different meteorites. The results given are the average values for the different specimens of the same meteorite. Each sample was analysed several times with an instrument precision of $\pm 0{\cdot}01$ per cent. The results obtained for the nine separate preparations from the Bella Roca meteorite (meteorite no. 1, Table 1) are given in Table 2 to show possible variations in, and reproducibility of the S^{32}/S^{34} for a single meteorite. The standard deviation in the S^{32}/S^{34} ratio for the set is seen to be $\pm 0{\cdot}004$ indicating a reproducibility of better than $\pm 0{\cdot}02$ per cent. Certainly little or no variation in S^{32}/S^{34} ratio is indicated within a single meteorite.

Since the absolute value of the S^{32}/S^{34} ratio is not known to better than $\pm 0{\cdot}5$ per cent, the assignment of an absolute value for the S^{32}/S^{34} ratio for meteoritic sulphur is somewhat arbitrary. The average S^{32}/S^{34} ratio of 22·22 reported for meteorites

Table 1. Sulphur isotope abundances in meteorites

No.	Locality	Type	No. of separate specimens investigated	S^{32}/S^{34}*	S^{34} ‰
1	Bella Rocca, Mexico	Iron (Med. Octahedrite)	9	22·230	−0·2
2	Bear Creek, Colorado, U.S.A.	Iron (Fine Octahedrite)	3	22·228	−0·1
3	Cambria, New York, U.S.A.	Iron (Fine Octahedrite)	3	22·223	+0·1
4	Joe Wright Mnt., Arkansas, U.S.A.	Iron (Med. Octahedrite)	3	22·223	+0·1
5	Duchesne, Utah, U.S.A.	Iron (Fine Octahedrite)	3	22·221	+0·2
6	Wichita, Texas, U.S.A.	Iron (Coarse Octahedrite)	1	22·227	−0·1
7	Canyon Diablo, Arizona, U.S.A.	Iron (Coarse Octahedrite)	4	22·220	+0·2
8	Cumpas, Mexico	Iron (Med. Octahedrite)	1	22·227	−0·1
9	Brenham Co., Kansas, U.S.A.	Iron-stone (Siderolite)	1	22·232	−0·3
10	Indarch, U.S.S.R.	Stone (Carbonaceous Chondrite)	3	22·227	−0·1
11	Hugoton, Kansas, U.S.A.	Stone (Breciated Chondrite)	1	22·222	+0·1
12	Gladstone, New Mexico, U.S.A.	Stone (Veined Chondrite)	2	22·222	+0·1
13	Alamagordo, New Mexico, U.S.A.	Stone (Black Chondrite)	2	22·229	−0·2
14	Waterville, Wash., U.S.A.	Pallisitic (Troilite Nodules)	1	22·223	+0·1
15	Mt. Sterling, Australia	Aerolite	2	22·229	−0·2
16	Xiquipilco, Mexico	Iron	1	22·229	−0·2
17	Monahans, Texas, U.S.A.	Iron	1	22·221	+0·2
		Average		22·225	

* Instrumental precision ± 0·01 per cent.

Table 2. Sulphur isotope abundances of troilite from Bella Roca meteorite (separate preparations)

Specimen	Date prepared	S^{32}/S^{34} Ratio*
1	1 April	22·227 ± 0·002
2	1 April	22·232 ± 0·002
3	1 April	22·232 ± 0·002
4	1 April	22·227 ± 0·002
5	28 April	22·227 ± 0·002
6	28 April	22·237 ± 0·002
7	31 July	22·232 ± 0·002
8	31 July	22·225 ± 0·002
9	1 August	22·232 ± 0·002
		22·230 ± 0·004†

* Instrument precision ±0·01 per cent.
† Standard deviation = 0·004.

Table 3. Sulphur isotope abundances of two meteorites compared

Meteorite	Sample no.	Method of SO_2 preparation	S^{32}/S^{34}*	Average of duplicate runs	δS^{34} ‰ average-value
Monahans, Texas, U.S.A. (Iron)	1	Direct burning of troilite	22·219	22·220	
	2	Direct burning of troilite	22·222		+0·19
	3	Burned as Ag_2S	22·224	22·221	
	4	Burned as Ag_2S	22·218		
Xiquipilco (Iron)	1	Direct burning of troilite	22·228	22·226	
	2	Direct burning of troilite	22·224		−0·18
	3	Burned as Ag_2S	22·231	22·231	
	4	Burned as Ag_2S	22·232		
		Difference between two meteorites—			0·37 ± 0·15‰

* Instrument precision ±0·01 per cent.

by Macnamara and Thode (1950), was based on a comparison of meteoritic sulphur with Park City, Utah, pyrite which had been used as a standard and assigned a value of 22·12 by Thode *et al.* (1949). The present value of 22·225 is based on a similar comparison. As pointed out earlier, the exact value assigned to the S^{32}/S^{34} ratio for meteorites is not important, providing the sulphur isotope ratio for any given sample is expressed relative to the sulphur isotope ratio for meteorites as a δ-value defined by equation (1) above.

Table 3 gives the detailed results obtained for samples 16 and 17 of Table 1. In each of these cases, four determinations were made, two in which the SO_2 samples used for isotopic analysis were prepared by the direct burning of the

troilite from the meteorite and finally, two by the burning of Ag_2S previously prepared from troilite. These results show the reproducibility of duplicate samples and indicate that the two methods of preparation of SO_2 give the same result. Finally, the results of Table 3 would suggest that the small difference in the sulphur isotope ratio shown, for example, between meteorites 16 and 17 in Table 1 is significant.

The results of Table 1 show that the S^{32}/S^{34} ratio for meteoritic sulphur is remarkably constant, the total spread for seventeen meteorites being of the order of 0·4 ‰. This is less than 1·8 ‰ and 2·2 ‰ spreads shown by Macnamara and Thode (1950), and Ault and Kulp (1959), respectively, but is consistent with the results of Vinogradov (1958), who gives identical values for eleven meteorites ($S^{32}/S^{34} = 22{\cdot}20$) to four significant figures, indicating variations could occur in the fifth place.

It is interesting that the stones, including the carbonaceous meteorite Indarch have S^{32}/S^{34} ratios within $\pm 0{\cdot}2$ ‰ of the average for all meteorites. The carbonaceous meteorites are of particular interest because of their peculiar structure and because they contain up to 2 per cent carbon, from 1 to 2 per cent material and up to 12 per cent water. Actually, the Indarch meteorite contains only 0·7 per cent carbon and 0·9 per cent water, which is considerably less than most carbonaceous meteorites. These meteorites show an appreciable variation in both D and C^{13} content (Boato, 1954).

We can therefore conclude that the S^{32}/S^{34} ratios for meteorites of all types are remarkably constant and fall in very narrow limits, however, small variations in isotope ratio between meteorites are indicated, probably of the order of $\pm 0{\cdot}2$ ‰. The question remains as to whether the S^{32}/S^{34} ratio for meteorites is indeed the primordial ratio for terrestrial sulphur as suggested by Macnamara and Thode. To date there is no direct evidence against this view and considerable evidence is building up to support it.

Average S^{32}/S^{34} *ratio* (*earth crust and mantle*)

It is, of course, very difficult to determine the average S^{32}/S^{34} ratio for the earth's crust and mantle. In sedimentary deposits and in the oceans, sulphates are, in general, highly enriched and the sulphides depleted in the heavy isotopes of sulphur. From the rough data available on the relative proportions of sulphate and sulphide in the sediments, the weighted average of the S^{32}/S^{34} ratio is found to be close to that for meteorites ($\delta = 0$), although Ault and Kulp (1959) estimate this average to be enriched in the heavy isotope ($\delta = +3{\cdot}6$). Considering the large variations in the S^{32}/S^{34} ratios in sedimentary rocks $\sim$100 ‰ and the rough estimates available for the relative amounts of sedimentary sulphides and sulphates in the earth's crust, $\pm 3{\cdot}6$ ‰ is perhaps as close as one could expect to come to the base level using this approach.

As suggested by Macnamara *et al.* (1952), sulphides from juvenile igneous origin are most likely to have the primary sulphur isotope composition. In particular, the primary sulphides of massive plateau basalts, or of the dunites and gabbros of large scale intrusions should give the best indication of the primordial sulphur isotope ratios for the earth since many of these magmas are of deep-seated

origin and may originate from the earth's mantle. The early results showed that there was a considerable spread in the S^{32}/S^{34} ratio for sulphides from igneous rock occurrences, and that although the values obtained overlapped the value given for meteoritic sulphur, there was a preponderance of samples with slight enrichment in S^{34} ($\delta = +3$ ‰). They suggested the possibility of some isotope fractionation during the crystallization of the magma.

Vinogradov (1958) reported similar fluctuations in the isotopic composition of sulphides in acid and basic igneous rocks with the more acid rocks showing in general the greatest enrichment in S^{34} ($+\delta$-value). However, for ultra basic rocks, such as pyroxenites and dunites, he obtained a fairly constant sulphur isotope composition corresponding to the composition of cosmic sulphur (meteorite). He assumes that the average terrestrial sulphur is the same as meteoritic, and suggests that the acid and basic rocks formed by the differentiation of ultra basic dunites become slightly enriched in the heavy isotope of sulphur in processes of magmatic and fractional crystallization.

Ault and Kulp disagree with these conclusions and on the basis of the average S^{32}/S^{34} ratios for sulphides from a limited number of mafic rocks ($\delta = +2{\cdot}3$ ‰) granitic plutonic rocks including pegmatites ($\delta = +3{\cdot}6$ ‰) and hydrothermal magmas ($\delta = +4{\cdot}1$ ‰) reported in the literature, conclude that the average sulphur isotope ratio for the earth's crust and mantle is $\delta = +3{\cdot}6$ ‰ rather than $\delta = 0$ ‰.

However, this conclusion is based on very limited data. Furthermore, although Ault and Kulp weighted their average according to the estimated proportion of sulphur in mafic and plutonic rocks as well as in hydrothermal deposits, the isotope ratios within each classification are often based on the analyses of single samples from large massive intrusions and, of course, are not weighted according to sulphur isotope distribution and sulphur content in these intrusives. It seems clear therefore that we must have a detailed study of each intrusive before an average sulphur isotope ratio can be established.

Several years ago, Thode and Dunford made a study of the sulphur isotope distribution in the Sudbury, Ontario, and Stillwater, Montana, intrusives. These results showed the magmatic sulphides and sulphides in the basic rocks in the basal zone of the differentiated intrusives to have a S^{34} δ-value of $\sim$0. The sulphides collected from the norite and micropegmatite, on the other hand, showed a steady increase in the S^{34} content in passing from the basic to acidic rocks in the intrusive, the micropegmatite having a value of +6. Also, Wanless *et al.* (1960), made a detailed study of the Yellowknife, Canada, area. Although this is a complex, metamorphosed region, the sulphur isotope studies showed a similar trend. More recently, samples selected from the Insizwa sill in South Africa were investigated in this laboratory (Shima, Gross and Thode, unpublished work, McMaster University, Hamilton, Ontario). This is a differentiated intrusive where the various stages of crystallization are well defined and where there is little evidence of associated rock having been introduced into the magma. Rock and mineral samples taken at various depths in the Insizwa sill, starting with the basal zone and up through the central zone gabbro, showed a one to one correspondence between sulphur isotope ratio and acidity of rock. The S^{34} δ-values ranged from $-2{\cdot}6$ at

the basal contact to +3·6 at the top of the gabbro of the central zone over a total rock thickness of ~4000 ft.

To obtain an average S^{32}/S^{34} ratio for the Insizwa intrusive one must, of course weight the results obtained for each sample according to the percentage of sulphur and thickness of rock represented by each sample. In this connexion, it should be pointed out that the sulphur content decreases markedly with the acidity of the rock and is, in general, low for granites. This means that the more acid rocks will not have the same weight in determining the average isotope ratio as the basic

Table 4. Sulphur isotope abundances in magmatic sulphide ores

Ore	Ref.	No. of samples averaged	S^{34} ‰
Sudbury Ni erruptive (Ontario)	(1)	10	+1·0
Stillwater Complex (Montana)	(1)	2	+0·35
Insizwa Sill (South Africa)	(2)	3	−2·6
Average			−0·4

(1) Thode, Dunford and Shima, unpublished work, McMaster.
(2) Shima, Gross and Thode, unpublished work, McMaster.

rocks which may contain up to ten times as much sulphur. Although further quantitative data are being obtained, it is clear in the case of the Insizwa sill that the average S^{32}/S^{34} ratio will be within 1 p.p.m. of the meteoritic value. Many such intrusions will need to be studied in detail before we can definitely say that the average S^{32}/S^{34} ratio for the mantle differs significantly from the value for meteoritic sulphur.

Magmatic sulphides are often associated with basic rocks at the base of a well differentiated magmatic deposit. These sulphide melts have a limited miscibility with the silicate phases and separate out simultaneously or follow the crystallization of olivines and dunites. Table 4 gives the isotopic abundances of three such magmatic sulphide deposits which belong to the pentlandite–pyrrhotite paragenesis. These results suggest that there is no significant difference in isotope ratio between sulphur of magmatic sulphides associated with ultra basic rocks and of meteorites.

Rafter *et al.* 1958a, Rafter *et al.* 1958b, Sakai 1957, Sakai and Nagasawa 1958, and others, have studied the distribution of sulphur isotopes in materials evolved from volcanoes and fumaroles as well as in the volcanic materials found around volcanoes. The variations found in the sulphur isotope ratios for extrusive materials are much more widespread than those found for massive igneous intrusions. This is undoubtedly due to isotopic exchange processes which are possible in the liquids and vapours issuing forth from the volcanoes. For example the exchange reaction

$$S^{32}O_2 + H_2S^{34} \rightleftharpoons S^{34}O_2 + H_2S^{32} \qquad (4)$$

has been studied by Cragg at various temperatures. He finds that even at 1000°C there is an appreciable isotope effect ($\alpha = \sim 1{\cdot}005$) favouring S^{34} in the SO_2. This

could very well account for the high S^{34} enrichment reported for some sulphates found around volcanoes. However, the warm waters around volcanoes are also known to contain sulphate reducing bacteria and considerable sulphur isotope fractionation could occur in the reduction process.

Because of the wide spread in S^{34} δ-values for the various forms of volcanic sulphur, it is most difficult to establish an average S^{32}/S^{34} value for volcanic sulphur. Rafter sampled the discharge gases from fumaroles on the volcano, White Island. He identified sulphides and polythionates as well as elemental sulphur and sulphate in these gases. The average δ-values for the various forms of sulphur collected from five fumaroles varied from +6·3 to −3·6 and the overall average for sulphur discharged from the fumaroles was found to be +3·0 ‰. Considering the possible loss of sulphur and possible exchange processes above and below the vents, this value is indeed close to the meteoritic value.

Sea water sulphate

Table 5 gives the S^{32}/S^{34} ratio and δ-value relative to meteoritic sulphur for

Table 5. Sulphur isotope abundances in sea water sulphate

Position and date collected	Depth (m)	δS^{34} ‰*	
Atlantic Ocean			
22°00′ N 30°00′ W	(3 samples)		
14 Feb., 1952	10, 683, 1213	+19·9	
0·9°25′ N 20°15′ W	3 samples		
28 Feb., 1952	1, 700, 1553	+20·2	
13°00′ N 38°58′ W	3 samples		
4 March, 1952	23, 651, 1600	+20·6	
16°24′ N 38°58′ W	3 samples		
31 March, 1952	21, 636, 1432	+20·1	
16°00′ N 46°08′ W	3 samples		
2 April, 1952	24, 975, 1838	+20·5	
11°59′ N 56°03′ W	3 samples		
9 April, 1952	43, 670, 1615	+20·0	
19°30′ N 64° W	surface	+20·3	Average 20·23
1954			
Pacific Ocean			
39°23′ N 129°55′ W	2 samples		
1950	1 and 2500	+20·8	
25°31′ N 119°46′ W	2 samples		
1950	1 and 2500	+19·3	
Pacific Naval Lab. No. 29	180	+19·8	
Off Mexico, 1954	surface	+20·3	
New Zealand, Wellington Area, 1956	surface	+19·6	Average 19·9
Arctic Ocean			
Resolute Bay, 1950–1951	surface	+19·8	
Alexandria Fjord, 1954	surface	+20·2	
Beaufort Sea, 1954	surface	+20·1	
Wellington Channel	surface	+20·4	Average 20·1
	Average	+20·1 ± 0·3	

* Instrument precision ±0·01 per cent.

samples collected from sixteen different locations in the Atlantic, Pacific and Arctic Oceans. In many cases, two and three samples were obtained at various depths. These samples did not show any correlation between isotope ratio and depth and the values for the various depths have been averaged for each location in Table 5.

The results show that the sulphate in the three oceans is remarkably uniform in isotope ratio with an average δ-value of $+20{\cdot}1 \pm 0{\cdot}3$ per mil. These results are in good agreement with a similar study reported by Ault and Kulp (1959) who, on the basis of some twenty-five samples from nine different locations, reported present-day sea water to have an average S^{34} δ-value of $+20{\cdot}7$ ‰ $\pm 0{\cdot}5$ (δ-value calculated according to equation 1 using their published S^{32}/S^{34} ratios).

Table 6. Sulphur isotopic abundances in freshwater lakes and ocean inlets (sulphates)

Source of sulphate	Depth	S^{34} ‰
Fresh Water, Lake Erie, Canada	Surface	+10
* Tokyo Bay	—	+14
Saanich Inlet, British Columbia	100 m	+19
Ocean (average value Table 4)		+20·1

* Value given by H. Sakai (1957).

Table 6 shows the S^{34} content of a large fresh-water lake system and of two ocean inlets fed by rivers in comparison to that of the sea. It is not surprising to find intermediate S^{34} δ-values in regions where fresh water and sea water mix.

Table 7 gives the sulphur isotope abundances of some samples of sulphate and sulphide derived from sea water. Columns 4 and 5 give the δ-values relative to meteorites and sea water sulphate, respectively. It is seen from Table 7 that the sulphate occluded in a present-day sea shell has the same isotopic composition as the sulphate in the sea. This result suggests that where evidence exists that the isotopic composition of certain ancient marine shells has been preserved, the sulphur isotope ratio found might be taken as the value for the ancient sea itself. It is interesting that two gypsum evaporites currently forming from sea water, one off the coast of Texas and the other from an inlet off the Pacific extending into a desert in Peru, have sulphur isotope ratios almost identical with that of sea water. (It means there are regions in the world to-day where evaporites are formed from a sea-water source with the same sulphur isotope ratio as that of the sea.). It is well known, of course, that anhydrite and gypsum deposits, in general, have a wide range of sulphur isotope ratios, Macnamara and Thode (1950), Ault and Kulp (1959). Since this spread in values occurs for evaporites from the same geological period, two questions arise: (1) What was the isotope content of sea water at a particular point in geological time? (2) What isotope fractionation processes are responsible for the wide range of sulphur isotope ratios found for evaporites of a particular period?

Studies of the sediments of the Uinta Basin (Harrison and Thode, 1958a), have shown that in an enclosed lake or sea, such as prevailed during the sedimentation period (Tertiary), large-scale sulphur isotope fractionation occurred continuously in time, probably due to the bacterial reduction of sulphate. Since the H_2S

produced in this process is depleted in S^{34}, the sulphate remaining becomes richer in this isotope. Such a biological process might also account for the wide range of isotope ratios found for anhydrite and gypsum deposits formed from shallow inland seas.

In the case where the fresh-water sulphate flowing into a large enclosed shallow sea is negligible and that the main source of sulphate is from continuous or intermittent contact with the sea, then all evaporites formed would either have the

Table 7. Sulphur isotope abundances of sulphates and sulphides derived from sea water

No.	Sample	Description of source	δS^{34} ‰ (re meteorites)	δS^{34} ‰ (re sea water)
1	$CaSO_4$	Present day sea shell	+20·4	+0·3
2	$CaSO_4 \cdot 2H_2O$ Gypsum	Evaporite on bottom of Boca de Virrila, Peru. (Pacific inlet into Peru desert) water depth 2 ft	+22·5	+2·4
3*	$CaSO_4 \cdot 2H_2O$ Gypsum	Currently forming in sea water (Laguna Madre, Texas coast)	+20·7	+0·6
4†	Sulphate	In rain water	+6·1	−14·0
4A‡	Sulphate	In rain water	+3·8	−16·2
5	Sulphides	In recent sediments Pedernales NE Venezuela. Formed by bacterial reduction of sea water sulphate in shallow muds.	+5·0	−15·0
6	Sulphate	Present day sea water (Average) Table 4	+20·1	0·0

* W. U. Ault and J. L. Kulp (1959).

† G. Ostlund (1959). Ostlund shows that rain water sulphate is 14‰ light in S^{34} as compared to sea water sulphate, see column 5. The δ-value in column 4 is adjusted to compare with sea water at +20·1.

‡ Sample sent to this laboratory by Ostlund.

same S^{32}/S^{34} ratio as the sea at the time of deposition as in the case of the two evaporites forming to-day (see Table 7) or they would show S^{34} enrichment due to bacterial action. If these were the main fractionation processes involved, then the evaporite with the lowest S^{34} content for a particular period should give the closest approach to the sea water isotope level at that time.

In the case of an inland sea or lake where a large proportion of the sulphate originates from river water, then sulphate in the evaporite could have an S^{34} content considerably less than that of the sea. This appears to be the case in the early stages of sedimentation in the Uinta Basin (Harrison and Thode, 1958a). The sulphur isotope studies in sediments of this basin showed a steady increase in S^{34} content with decreasing depth of sediment. In fact, the oldest sediments in the basin were found to be highly depleted in S^{34} ($\delta = 0$ or $-$) as compared to sea water to-day, whereas the youngest sediments were found to be highly enriched ($\delta = +35$). However, in the case of the Uinta Basin, it is well known from other

geochemical considerations that the sediments are non-marine in origin which would explain the low δ-values in the first sediments to be laid down. The interpretation of sulphur isotope distribution data in evaporites will be complicated by the fact that we have gypsum and anhydrite deposits which have been formed under marine, non-marine, and mixed conditions. It is therefore essential that the sulphur isotope data be interpreted in the light of other geochemical considerations. A detailed study is being made of the sulphur isotope distribution in the evaporites of the Williston Basin, both from a horizontal and vertical point of view. It is hoped that this study will add additional information concerning the ancient seas and evaporation processes.

Samples 4 and 5, Table 7, are of considerable interest in connexion with sulphate geochemistry. The sulphides in the recent sediments are undoubtedly formed by the bacterial reduction of sea water sulphate in the shallow muds. Thode *et al.* (1960), showed that the sulphides in the recent sediments of Northeastern Venezuela have an average S^{34} content of $\delta = +5$ as compared to $+20$ for the source sulphate in the sea. This means an average kinetic isotope effect of 15 ‰ in the bacterial reduction process which is in the range of values found in laboratory experiments where the bacterial reduction was carried out under less than optimum conditions.

The sulphur isotope ratio of rain water, samples 4, and 4a Table 7, can also be related to the sea water level. The question of the origin of rain water sulphate and of the geochemical circulation of sulphur generally, has been discussed by Goldschmidt (1954), Clarke (1924), Conway (1942), and more recently, by Eriksson (1960). The large amounts of sulphur discharged by rivers cannot be explained by weathering, and geochemical data rule out volcanoes, fumaroles and fuel combustion as appreciable sources of this sulphur. The bacterial reduction of sea water sulphate and the loss of H_2S to the atmosphere where it is easily oxidized appears to be the answer. Conway (1942), estimates that the total sulphate carried down to the sea by rivers is three times that expected from rock weathering and concludes that the extra sulphate would appear to be largely circulation of H_2S from the sea to the atmosphere and its return in rain as sulphate.

Conway (1942) makes calculations to show that H_2S could possibly escape from very shallow seas, and Eriksson (1960) points out that H_2S would obviously escape from intertidal flats which cover an appreciable area and where conditions for H_2S production by bacterial action is ideal. The depletion in S^{34} of the sulphate in rain water of about 15 ‰ with respect to sea water (see sample 4, Table 7) provides evidence in favor of the sulphate–hydrogen sulphide sulphur cycle proposed by Conway, Eriksson, and others, since this is about the depletion one would expect if the bacterial reduction of sea water sulphate is involved in the cycle.

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Rates of oxidation of petroleum asphaltenes and other bitumens by alkaline permanganate*

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Abstract—Rate of oxidation by alkaline permanganate has been used by a number of investigators for comparison of coals, oil shales, and related natural bitumens, and to provide an insight into their molecular structures. The method is equally applicable to petroleum asphaltenes. To facilitate additional studies, a semi-automatic titrating and recording apparatus has been designed and constructed. Twenty-six samples, comprising coals, oil shale, gilsonites, manjak or glance pitch, natural graphite, asphaltenes from crude oils and refinery fractions, and the insoluble carbonaceous material in marine and non-marine rocks, have been examined. Oxidation rates of the coals and petroleum asphaltenes vary by a factor of more than 500 and in general show a rough correlation with the oxygen content of the organic material.

Introduction

In recent years, much progress has been made toward an understanding of the composition of crude oils. A fairly detailed picture of the array of hydrocarbons which make up the naphtha to gas oil fraction now is available. Current researches are rapidly doing the same for the lower molecular weight sulfur-containing compounds and for the nitrogen-containing compounds. The remaining large fraction of crude oils is the asphaltics and of the chemical structure of these substances far less is known.

In this paper, the term "asphaltics" will be used to denote that fraction of crude oils which is non-hydrocarbon in composition, i.e., contains, in addition to carbon and hydrogen, oxygen, nitrogen and sulfur; is highly colored, possessing an absorption spectrum in the visible-ultraviolet characterized by gradually increasing intensity of absorption with decreasing wavelength and absence of structure and is essentially insoluble in liquid propane at ambient temperatures. Observations in this laboratory, some of which are reported in a preliminary manner in a previous paper (Erdman, *et al.*, 1958) have led to the working hypothesis that within a given crude oil the asphaltic fraction is comprised of molecules of similar chemical structure but which vary, in molecular weight, from a thousand or so to many thousands. Solubility in the common hydrocarbon solvents, including crude oil itself, decreases with increasing molecular size. In fact, it is believed that the upper limit of molecular weights of the asphaltics observed in crude oils is determined by solubility and that higher molecular weight material of petroleum asphaltic character is to be found in the source bed rocks. Support for this viewpoint is provided by the finding, reported herein, that the oxidation rate for the insoluble carbonaceous fraction from a petroleum source rock corresponds closely to that for the asphaltene fraction of the crude oil.

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While the lower members of the asphaltic series are viscous liquids at room temperature, the higher members are solid with softening points in the range of 160 to more than 200°C. From an experimental standpoint, it is convenient to divide the asphaltics into two fractions based on solubility in *n*-pentane. The soluble fraction is usually a viscous liquid. The insoluble fraction is known as asphaltenes and is usually a powdery solid. This terminology is used throughout this paper.

The general structure of the asphaltic molecule has been pictured as a fabric consisting of clusters of condensed, largely aromatic, rings linked together with aliphatic chains (Yen *et al.*, 1960). Experimental evidence for this picture is derived from a variety of instrumental methods, such as X-ray, NMR, infrared, and computational procedures based on elementary analysis and density.

This picture of the structure of the asphaltic molecule bears close resemblance to that which has been proposed for coal (Dryden and Griffiths, 1953; Given, 1960). In fact, published X-ray, infrared, ESR and NMR data for coal are quite similar to corresponding data for petroleum asphaltenes. (Friedel, 1959; Friedel and Queiser, 1956; Ergun and Tiensuu, 1959). However, a sharp distinction between these two substances is found in their chemical behaviour. In the previous paper, preliminary investigations of the behaviour of several petroleum asphaltenes to oxidation with alkaline potassium permanganate were reported. The method used was that developed by Bone and co-workers (1930; 1935; 1936) at the University of London in which a suspension of bitumen in dilute aqueous alkali is titrated with alkaline permanganate solution. To determine whether rate data for substances examined in this laboratory could be compared with data for other substances reported in the literature, a sample of the Colorado Green River oil shale was run. The curve obtained was reasonably close to that reported for the same material by Robinson, Heady, and Hubbard (1953). While significant differences were observed between the rates of oxidation of the three petroleum asphaltenes, the striking feature was that these rates of oxidation apparently were much slower than those reported for other bituminous substances, namely, oil shale kerogens, algal shales and limestones, peats, and coals (Dancy and Giedroyc, 1950; Down and Himus, 1941). Examination of the oxidation products also indicated a generally higher yield of non-volatile, non-oxalic acids in the solubilized portions. Interpretation of these findings for petroleum asphaltenes on the basis of data for compounds of known structure as determined by Randall and co-workers (1938) and by Robinson and co-workers (1953; 1956), was attempted.

The apparently remarkable resistance to oxidation by permanganate, observed for the three petroleum asphaltenes, stimulated the desire to perfect the oxidation rate method as an exploratory tool, to examine a larger number of native petroleum asphaltenes, to determine the effect of refining conditions and to compare, under conditions as comparable as possible, their rates with other solid natural bitumens including the black, insoluble material present in rocks believed to be source beds of petroleum.

Discussion

The procedure as described by Bone and co-workers, and used by the present authors in their earlier studies, contains several obvious handicaps and uncertainties. Briefly, it consists of suspending 1 g of the powdered asphaltene in 100 ml of a

dilute boiling solution of potassium hydroxide and adding, in 2 ml increments, a 3 per cent solution of potassium permanganate by means of a dropping funnel. The time of addition of the first 2 ml of permanganate solution is taken as time zero. As soon as the violet color of the permanganate disappears from the reaction mixture, a second increment of oxidant is added and so on. Periodically, during a run, the original volume of the suspension is restored by distilling off a volume of water equal in volume to the permanganate solution added. The rate of oxidation gradually decreases with time and is arbitrarily discontinued after approximately 100 hours. The time-consuming nature of the operation is, of course, obvious, as well as the difficulty in observing the disappearance of the violet color in a suspension of a black material. Further, the concentration of oxidant does not remain constant throughout the determination but varies between 0·06 per cent and zero. Since a considerable quantity of the sample is oxidized in the time necessary to determine the curve by the incremental method, the rate of consumption of oxidant decreases and the curve is concave upward. Further, there are the uncertainties as to the effects of variation in the method of sample preparation. In the previous paper, the effect of one experimental variable, particle size, was explored. To expedite the study, the titration period was decreased to one hour and the size of the increment of potassium permanganate solution added decreased to 0·05 ml. In so doing, gains were made both in a saving of time and in having the curves assume the form of essentially straight lines after a short initial induction period. The experimental difficulty of following the decrease in the purple color and determining the proper time for the addition of the next increment of permanganate was increased, however.

To overcome the procedural difficulties, a semi-automatic titration procedure was developed whereby the concentration of oxidant would be held constant throughout the experiment and the consumption of oxygen could be recorded as a continuous curve. To avoid loss of liquid through evaporation, a constant temperature, somewhat below the boiling point of the reaction mixture, was adopted.

The sensing and control of the concentration of oxidant is complicated by the fact that in the course of oxidation of organic material by permanganate, the latter is reduced first to manganate and then to manganese dioxide. This complication was overcome in the present work by adopting the procedure of Stamm (1934) whereby the half-reaction, permanganate to manganate only is used, the further reduction of the manganate ion being stopped by precipitation with barium. With the apparatus and procedure as described in greater detail in the Experimental section, it is possible to obtain in a half-hour accurate curves approximating straight lines from the slopes of which numerical rates could be determined. Tests of the apparatus using aliquots of the same samples indicated a high degree of instrumental reproducibility.

Factors involved in sample preparation which might affect the oxidation rate were examined. In the previous paper, it was shown that particle size and wettability were second order variables. Additional studies using the rapid titration procedure showed that removal of the last traces of hydrocarbon oils was desirable: for the petroleum asphaltenes, it was found sufficient to reprecipitate them from benzene. To achieve constancy in texture, all samples were freeze-dried out of

benzene solution or suspension and then screened to a constant size range. To achieve complete wetting, shaking with water for a fixed period of time prior to the titration was adopted. Variation in the length of time that the bitumen was in contact with the alkali prior to initiation of the titration was also found to alter the rate slightly. To minimize the effects, the alkali was added and a definite time allowed to elapse before the titration. A fixed rate of heating to titration temperature also was adopted. The control runs established that trace metals, such as vanadium, nickel, and copper, either in the form of inorganic salts or as porphyrin complexes, had no effect on the oxidation rate of an asphaltene. However, sulfide in the form of iron pyrite is oxidized at a sufficiently high rate to represent an interfering factor. In the case of those bitumens which could be completely dissolved in benzene, pyrite was eliminated by filtration or, better, by centrifugation. In the case of the coals, it proved feasible to recognize pyrite by X-ray examination, to estimate its quantity from the amount of iron present, and to correct the oxidation rate curve accordingly. Since the rate of oxidation of the coals is high, the correction due to pyrite was in most instances negligible or, at least, small. Pyrite proved to be a more serious problem where attempts were being made to determine the oxidation rate of the insoluble carbonaceous material contained in rocks, particularly the La Luna limestone. Here, the concentration of pyrite was very high and the oxidation rate of the organic matter rather slow. The problem was solved by reducing the amount of pyrite by density separation, although the process usually proved rather tedious. The organic material and the pyrite seemed to be intimately associated in the finer grained fractions. An improvement in the separation was achieved by subjecting the suspensions to ultrasonic vibrational energy prior to centrifugation. A control whereby a suspension of petroleum asphaltene was subjected to the same ultrasonic treatment, however, revealed a sharp increase in oxidation rate. On the suspicion that the ultrasonic energy might be destructive to the molecular fabric, this step, desirable as it may have been, was abandoned. Details for the preparation of each type of sample are provided in the Experimental section.

Experimental

Apparatus

The principle of the apparatus used for the semi-automatic determination of oxidation rate of solid bituminous material is shown in schematic form in Fig. 1 and consists of four major sections: a reaction vessel, a motor-driven hypodermic syringe for dispensing oxidant, a redox control system which serves to maintain a constant concentration of oxidant in the reaction vessel and a system for recording the consumption of oxidant as a function of time. The circuit for maintaining constant temperature in the reaction vessel is conventional and is not shown in the diagram.

The all-glass reaction vessel resembles a resin reaction kettle with a volume to the flange of 300 ml. The flanged lid has a centrally located $\overline{\$}$ 29/42 female joint through which is attached a water-cooled Precision Bore stirrer bearing and stirrer. Arranged in a half circle around the central taper is a small water-cooled condenser sealed directly to the lid, sleeves for the calomel and bright platinum electrodes, and a $\overline{\$}$ 10/30 female joint to accommodate a contact thermometer for control of temperature. Oxidant is introduced through the condenser by means of a U shaped tube, 1 mm i.d., which connects to the barrel of the motor driven syringe through a small glass joint and extends below the surface of the liquid in the reaction vessel. Heat is provided by means of a Glas-Col mantle.

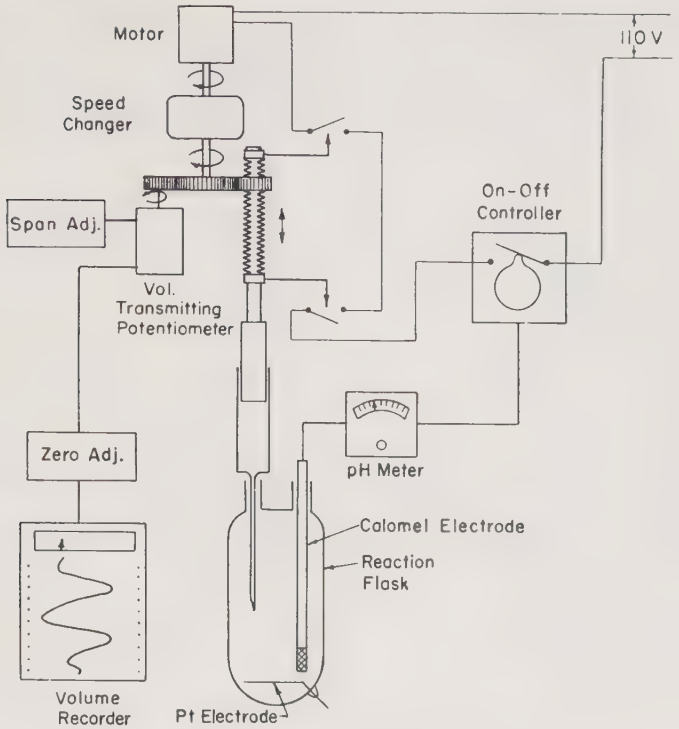

Fig. 1. Schematic plan of the apparatus for the semi-automatic determination of oxidation rates.

The power-driven hypodermic syringe for dispensing oxidant, i.e., the potassium permanganate solution, is shown in Fig. 2. Finer control in the dispensing of the oxidant was achieved by placing the hypodermic syringe in a vertical position with the outlet directed upward and connecting with the reaction vessel through a capillary U-tube as described above. The motor drive is activated by the redox control system, turning on when oxidant is required. Owing to the wide range in rates encountered, it proved necessary to place a speed-change box between the motor and the shaft driving the piston of the syringe. The latter is connected through appropriate gears to a potentiometer and voltage source, the output of which is a function of piston position. This voltage, fed to a strip chart recorder running at constant speed, provides a record of total oxidant added as a function of time.

The concentration of permanganate to be maintained in the reaction vessel is 3×10^{-4} molar, the redox potential of which corresponds to -375 millivolts. The potential between the calomel and bright platinum electrodes is measured with an L and N pH meter which feeds its signal to an L and N Type H set point controller, which, in turn, actuates the motor drive of the syringe.

For recording the volume of oxidant as a function of time, the signal from the recording potentiometer, geared to the drive for the hypodermic syringe, is fed to an L and N Type G single pen recorder. Details of the necessary circuit are shown in Fig. 3.

Preparation of sample

The asphaltene fraction of the native crude oils, the gilsonites and manjak (glance pitch), and the refinery fractions were prepared in the usual manner by precipitation with *n*-pentane. Precautions were taken to avoid exposure of the material to atmospheric oxygen. The freshly prepared asphaltenes were freed of residual oil by two further precipitations, each of which consisted of dissolving the material in 1·9 volumes of benzene and adding 10 volumes of pentane

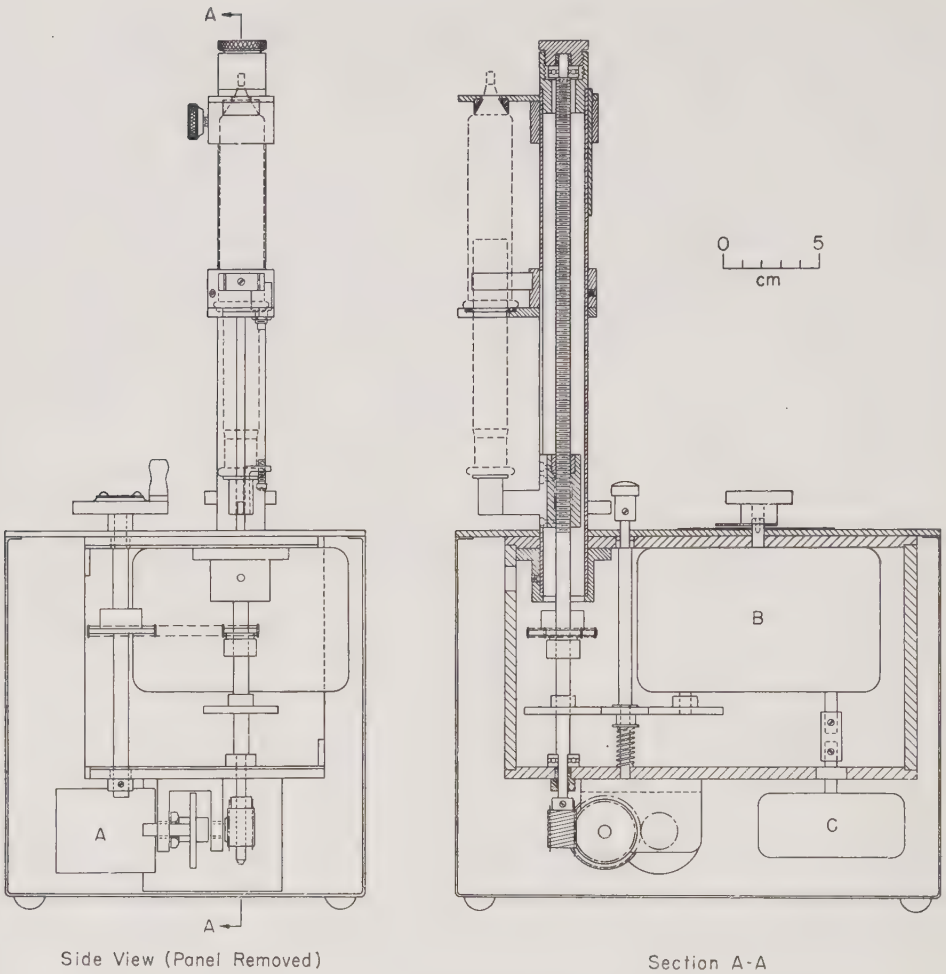

Fig. 2. Power driven hypodermic syringe for dispensing oxidant.
(A) Volume transmitting potentiometer. (B) Speed change box. (C) Motor.

with stirring. The precipitates were washed with pentane, vacuum dried at room temperature, weighed into freeze-drying flasks, dissolved in 17 volumes of benzene, and freeze-dried. The fraction of particle size between Nos. 100 and 270 U.S. Standard mesh were taken for the oxidation rate determination.

The coals and oil shale were crushed, ball milled with distilled water under nitrogen, and freeze-dried. The resulting powder was extracted with pentane, the residue suspended in 17 volumes of benzene, and freeze-dried. The residue was screened to provide the 100–270 mesh fraction.

The La Luna limestone, the non-marine carbonaceous shale, and the Green River oil shale, crushed, milled, freeze-dried, and extracted to remove oils, were screened to provide a <100 mesh fraction. The powdered material was treated first with cold 12 per cent hydrochloric acid to remove carbonates and then with cold 48 per cent hydrofluoric acid to dissolve silica and to decompose the clays. After thorough washing with distilled water, the residues were slurried with water and freeze-dried. The larger portions of the pyrite and insoluble acid aluminum fluorides were removed by flotation, the separation being promoted by high speed centrifugation. For the La

Luna limestone and the Green River oil shale, the suspending liquid was carbon tetrachloride; for the non-marine carbonaceous shale, a 1:6 mixture of acetone-bromoform was found to be the most effective. Approximately three consecutive separations were used to achieve the final products. The lighter organic, or floated material, was finally suspended in 17 volumes of benzene, freeze-dried, and screened to provide the 100–270 mesh fraction. An aliquot was analyzed for iron and the concentration of pyrite estimated for correction of the observed rate curve.

Determination of the oxidation rate

Two aliquots of each sample, prepared as above, each containing 0·85 g of organic carbon, were suspended in 100 ml of distilled water in 125 ml glass-stoppered Erlenmeyer flasks and

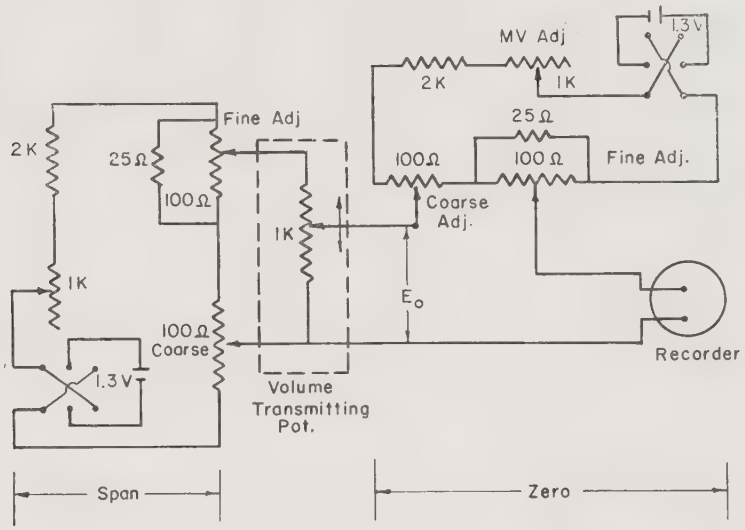

Fig. 3. Circuit for the recording of the volume of oxidant consumed as a function of time.

shaken mechanically for exactly two hours. The suspensions then were transferred quantitatively to the glass reaction vessel, 4·2 g of potassium hydroxide and 2 g of barium chloride dihydrate added, and the total volume of the mixture brought to exactly 200 ml by the addition of distilled water. Stirring and heating were begun immediately, the latter at a rate sufficient to bring the temperature to 78°C in 6 to 7 minutes. As soon as the controlled temperature was reached, the automatic titrator and recorder were activated. The titrating solution was 0·195 molar potassium permanganate prepared with distilled water. The titration was allowed to continue for 30 minutes unless the supply of oxidant in the hypodermic syringe became exhausted in a shorter period of time, as was usually true in the case of the coals.

To permit correction of the rate curves of those samples containing iron pyrite, rate curves for pyrite were obtained using 0·025 and 0·10 g of the pure mineral. Between these limits, it was assumed that the slope of the rate curve would increase linearly with the size of the pyrite sample.

Results

The oxidation rates for the samples prepared according to the procedure described in the Experimental section, corrected where necessary for pyrite, are recorded in Table I. Each value is the mean of at least two determinations.

It will be seen that the general conclusion drawn in the earlier paper, namely, that native petroleum asphaltenes are far more resistant to permanganate oxidation

Table 1. Oxidation rates of various bituminous substances

Number[1]	Sample	Rate[2]
	Shale–Non-Marine	
1	Insoluble carbonaceous material (Pennsylvania)	20
	Bituminous Coals	
2	Lower Freeport seam, Pennsylvania	20
3	Upper Freeport seam, Pennsylvania	10
4	Hanna seam, Wyoming	12
	Lignite	
5	Kincaid Mine, North Dakota	9·7
	Cannel Coal	
6	Lens above the Upper Freeport seam, Pennsylvania	3·5
	Oil Shale	
7	Green River, Colorado	1·5
	Gilsonites	
8	Tabor Vein, No. 5 Shaft, Big Bonanza Camp, Uinta County, Utah	0·11
9	Cowboy Vein, Utah	0·11
	Limestone–Marine	
10	insoluble carbonaceous material (La Luna, Venezuela)	0·12
	Petroleum Asphaltenes	
11	Ragusa, Sicily	0·11
12	Raudhatain, Kuwait	0·095
13	Mara, Venezuela	0·088
14	Lagunillas, Venezuela	0·083
15	Wafra No. 17, Kuwait-Saudi Arabia Neutral Zone	0·078
16	Wafra No. A-1, Kuwait-Saudi Arabia Neutral Zone	0·078
17	Burgan, Kuwait	0·065
18	Baxterville, Mississippi	0·045
	Manjak	
19	Bahia Honda Mine, Pinar del Rio, Cuba	0·078
	Graphite	
20	Natural, Ceylon	0·045
	Petroleum Asphaltenes from Refinery Fractions	
21	Straight run residuum, Mid-Continent type	0·180
22	Straight run residuum, California type	0·300
23	Straight run residuum, Venezuela type	0·078
24	Kuwait vacuum tower bottoms	0·070
25	Kuwait visbreaker tar	0·105
26	Kuwait hydrogenated vacuum tower bottoms	0·055

[1] See Figure 4

[2] Slope $= \frac{\text{volume of oxidant (ml of 0·195 molar } KMnO_4 \text{ solution)}}{\text{time (minutes)}}$. Corrected for residual pyrite where present.

than coals and oil shale, remains correct, the rates for the three bituminous coals averaging between 100 and 300 times those of the petroleum asphaltenes. Lignite appears to have only a slightly lower rate, while cannel coal, collected from a lens immediately above the Upper Freeport coal, has an oxidation rate of only one-third that of the closely associated bituminous coal. The Green River oil shale has an oxidation rate of about one-tenth that of the bituminous coals. The gilsonites and manjak, or glance pitch, on the other hand, fall within the range of the native petroleum asphaltenes, which, in themselves, differ in rate by only a little more than a factor of two.

The black, insoluble carbonaceous materials isolated from two rock types exhibited extremely different oxidation rates. The material isolated from the clay shale of Pennsylvanian age, located below the Pittsburgh coal seam and believed to be of fresh water origin, showed a rapid oxidation rate comparable to that for bituminous coals. On the other hand, the material isolated from the Lower Cretaceous La Luna limestone showed a much slower oxidation rate, approaching that of the asphaltene fraction of crude oils. The La Luna limestone is generally accepted as being the source of the Mara crudes. The similarity in oxidation rates between the oil-soluble Mara asphaltene and the insoluble fraction from the limestone is taken here as indicating like structure; solubility differences are attributed to lower and higher molecular weight ranges, respectively. These observations are believed to be significant in relation to the origin of these bitumens.

The asphaltenes from the refinery bottoms show little difference in oxidation rate from the native petroleums. The first two straight run residua have somewhat higher rates, but no examples of native Mid-Continent or California type petroleum asphaltenes have been studied as yet. On the other hand, the Venezuela straight run residuum resulting from a mixed Mara stock has a rate very close to that of the native Mara crude. In like manner, the three refinery fractions prepared from Kuwait crude fall within the range of the rates for the asphaltenes from the two native Kuwait crudes. The slow rate of oxidation of petroleum asphaltenes is strikingly evidenced by the fact that the most resistant, namely, the Baxterville, is oxidized at the same rate as natural crystalline graphite, which is believed to consist of sheets of condensed aromatic rings.

The extent to which oxidation rate correlates with the elementary chemical composition of the samples and such geological factors as the type and geological age of the producing formation are shown in Tables 2, 3, and 4. In Table 2 are provided the analytical values for carbon, hydrogen, oxygen, nitrogen, sulfur, ash, iron, vanadium, and nickel for the various samples studied. In Table 3, the elementary composition of the organic material has been approximated by normalizing the total of the percentages of carbon, hydrogen, oxygen, nitrogen, and sulfur to equal 100 per cent for each sample. In Table 4, are listed the eight crude oils from which the samples of native asphaltenes were prepared. Data are provided for the geographic locations from which these oils were obtained, the identity, where known, of the producing formation, the composition of the producing formation and its geologic age.

From the data in Table 2, it is evident that no correlation exists between oxidation rate and the amount of inorganic material or, more specifically, the

Table 2. Elementary and ash analyses for the bituminous substances oxidized

Sample	C	H	O	N	S	Ash	Fe	V	Ni
Shale—Non-Marine									
Insoluble carbonaceous material	33·4	3·1	8·0	1·00	1·18	48·82	1·35	—	—
Bituminous Coals									
Lower Freeport	77·0	5·7	8·1	1·42	1·72	5·55	1·07	0·009	0·005
Upper Freeport	79·9	5·5	7·3	1·65	0·69	4·34	0·35	<0·005	0·001
Hanna	65·9	6·1	17·4	1·17	0·58	6·35	0·45	0·005	0·001
Lignite									
Kincaid Mine	63·1	5·0	21·5	0·64	<0·04	9·05	0·26	0·010	0·0005
Cannel Coal									
Above Upper Freeport	56·4	4·3	6·3	1·07	1·61	30·33	1·31	<0·005	0·014
Oil Shale									
Green River	65·7	9·1	8·9	2·13	3·15	8·63	1·57	0·006	0·009
Gilsonites									
Tabor Vein	84·5	10·0	2·6	2·41	0·53	0·52	0·15	0·005	0·03
Cowboy Vein	84·1	9·6	1·8	3·43	0·43	0·00	0·011	0·002	0·0001
Limestone—Marine (La Luna)									
Insoluble carbonaceous material	78·0	6·1	7·6	1·13	6·87	5·34	0·63	0·53	0·084
Petroleum Asphaltenes									
Ragusa	81·7	8·8	1·8	1·47	6·31	0·66	0·040	0·008	0·0379
Raudhatain	80·9	7·9	1·8	0·82	7·70	0·42	0·125	0·039	0·0095
Mara	83·5	7·9	1·0	0·92	5·41	0·19	0·030	0·237	0·0262
Lagunillas	84·2	7·9	1·6	2·00	4·50	0·59	0·018	0·250	0·0370
Wafra, No. 17	81·7	8·1	1·2	0·55	7·90	0·63	0·053	0·044	0·0138
Wafra, No. A–1	81·8	8·1	1·5	1·03	7·80	0·70	0·053	0·050	0·0246
Burgan	82·2	8·0	0·6	1·70	7·60	0·10	0·027	0·044	0·0107
Baxterville	84·5	7·4	1·7	0·80	5·60	0·50	0·013	0·024	0·0026
Manjak									
Bahia Honda Mine	81·0	7·3	0·9	1·01	8·58	1·46	0·025	0·004	0·0206
Graphite									
Natural	99·1	0·5	0·1	<0·10	0·21	0·34	0·015	0·010	0·0045
Petroleum Asphaltenes from Refinery Fractions									
Straight run residuum—									
Mid-Continent type	87·7	6·6	1·6	0·90	0·75	1·34	0·031	0·028	0·0171
California type	83·8	7·8	3·6	1·87	1·16	0·00	0·069	0·009	0·0512
Venezuela type	83·9	8·0	1·7	1·16	3·86	0·49	0·008	0·150	0·0223
Kuwait vacuum tower bottoms	81·6	7·1	1·6	0·87	7·78	0·63	0·013	0·046	0·0146
Kuwait visbreaker tar	83·7	5·8	1·5	0·93	7·55	0·60	0·010	0·043	0·0179
Kuwait hydrogenated vacuum tower bottoms	83·3	5·1	2·7	1·06	6·82	1·01	0·023	0·043	0·0450

concentrations of the transition metals, iron, vanadium, and nickel. This conclusion tends to rule out the possibility that inorganic catalysis is a major factor in the oxidation rate observed for the organic fraction of the samples.

Comparison of the elementary composition of the organic fractions, provided in Table 3, shows little or no correlation between oxidation rate and the percentages of carbon, hydrogen, nitrogen, and sulfur. However, there appears to be a rough, direct correlation between oxygen content and oxidation rate as shown in Fig. 4. This relationship also holds reasonably well for the oxidation rates for pure compounds reported by Randall and by Robinson and their co-workers. The principal exception is the insoluble carbonaceous material from the La Luna limestone. Here it is possible that some oxygen may have been picked up during the many steps involved in the preparation of this sample, although if such proves to be the case, it must be concluded that the oxygen picked up during sample preparation is not present in a form that influences the oxidation rate.

As is shown in Table 1, the oxidation rates exhibited by the eight native asphaltenes prepared from crude oils vary by only little more than a factor of two However, in most instances, the differences in rates are beyond the experimental

Table 3. Content of carbon hydrogen, oxygen, nitrogen, and sulfur for the bituminous substances oxidized (normalized to 100%)

Sample	Per cent				
	C	H	O	N	S
Shale—Non-Marine (Pennsylvania)					
Insoluble carbonaceous material	71·5	6·6	17·2	2·14	2·53
Bituminous Coals					
Lower Freeport	82·0	6·1	8·6	1·51	1·83
Upper Freeport	83·9	5·9	7·8	1·77	0·74
Hanna	72·3	6·7	19·1	1·28	0·64
Lignite					
Kincaid Mine	69·9	5·5	23·8	0·71	0·04
Cannel Coal					
Above Upper Freeport	85·7	4·6	6·8	1·15	1·73
Oil Shale					
Green River	73·9	10·2	10·0	2·39	3·54
Gilsonites					
Tabor Vein	84·5	10·0	2·6	2·41	0·53
Cowboy Vein	84·6	9·7	1·9	3·45	0·45
Limestone—Marine (La Luna)					
Insoluble carbonaceous material	78·2	6·2	7·6	1·13	6·89
Petroleum Asphaltenes					
Ragusa	81·6	8·8	1·8	1·47	6·30
Raudhatain	81·6	8·0	1·8	0·83	7·77
Mara	84·7	8·0	1·0	0·93	5·49
Lagunillas	84·0	7·9	1·6	2·0	4·5
Wafra, No. 17	82·1	8·1	1·3	0·55	7·95
Wafra, No. A-1	81·6	8·1	1·5	1·03	7·78
Burgan	82·1	8·0	0·6	1·70	7·60
Baxterville	84·5	7·4	1·7	0·80	5·60
Manjak					
Bahia Honda Mine	82·0	7·4	0·9	1·02	8·69
Graphite					
Natural	99·1	0·5	0·1	<0·10	0·21
Petroleum Asphaltenes from Refinery Fractions					
Straight run residuum—					
Mid-Continent type	89·9	6·8	1·6	0·92	0·77
California type	85·3	8·0	3·7	1·90	1·18
Venezuela type	85·0	8·1	1·8	1·18	3·91
Kuwait vacuum tower bottoms	82·5	7·2	1·6	0·88	7·87
Kuwait visbreaker tar	84·1	5·9	1·5	0·93	7·58
Kuwait hydrogenated vacuum tower bottoms	84·1	5·1	2·8	1·07	6·89

limits of error. This fact was demonstrated in several cases by parallel preparation of asphaltene fractions from the crudes. The tabulation in Table 4 fails to show any correlation with geographic area or with geologic age of the producing formation. There does seem, however, to be an indication that the crudes containing the more readily oxidized asphaltenes are produced from limestone or dolomite formations,

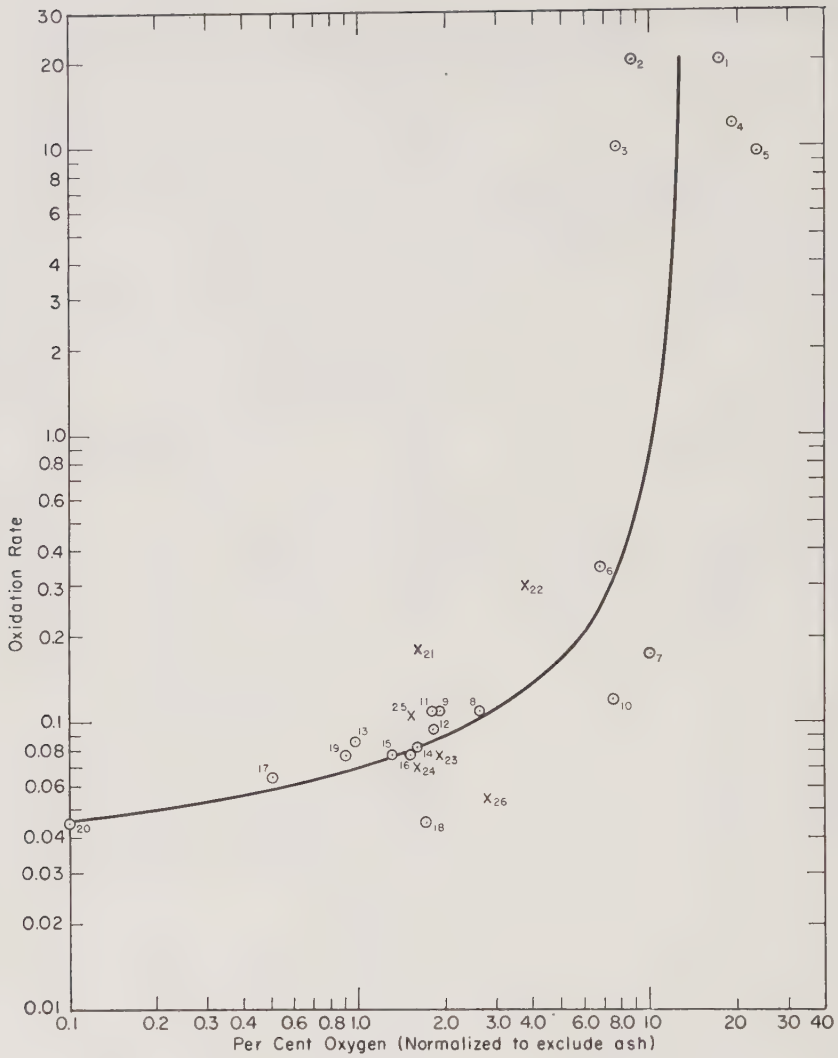

Fig. 4. Relation between the content of oxygen and oxidation rate. The identifying numbers correspond to those in the first column of Table 1. The circles represent fractions prepared from native bitumens and the X's those prepared from refinery fractions.

while the more resistant asphaltenes come from crudes produced from sands. Asphaltenes from many more crude oils would have to be studied before this correlation could be considered reliable.

Conclusion

A rapid, semi-automatic procedure has been devised for the determination of oxidation rate of solid organic materials, primarily natural bitumens, using alkaline potassium permanganate. Under the conditions of the determination, the resulting curves approximate straight lines, the slopes of which may be taken as the rates. Examination of twenty-six samples, comprising bituminous coals, oil shale,

Table 4. Geographic and geologic information pertaining to the sources of the crude oils from which the native asphaltenes were prepared

		Producing Formation		
Crude oil	Geographic location	Name	Composition	Geological age
Ragusa	Sicily	Taormina	fractured dolomite	Upper Triassic
Raudhatain	Kuwait	Mauddud	limestone	Middle Cretaceous
Mara	Venezuela	La Luna	fractured limestone	Lower Cretaceous
Lagunillas	Venezuela	Lagunillas	sandstone	Oligomiocene
Wafra, No. 17	Kuwait-Saudi Arabia Neutral Zone	First sand*	quartz sand	Middle Cretaceous
Wafra, No. A–1	Kuwait-Saudi Arabia Neutral Zone	Ratawi	oolitic limestone	Lower Cretaceous
Burgan	Kuwait	Burgan	sand	Middle Cretaceous
Baxterville	Mississippi, U.S.A.	Tuscallusa	sand	Upper Cretaceous

* Apparently corresponds to the Wara formation of Southeastern Kuwait.

gilsonites, manjak or glance pitch, native crude oil asphaltenes, natural graphite, and asphaltenes from refinery fractions is reported. It is noted that the coals and oil shale are rapidly oxidized, that the gilsonites, manjak or glance pitch, and the native asphaltenes exhibit a resistance to oxidation approaching that of asphaltenes from crude oil, and that the black, insoluble carbonaceous material in a non-marine shale and in a marine limestone, believed to be the source bed of a crude oil, exhibit rates of oxidation approximating coals and petroleum asphaltenes, respectively. Asphaltenes prepared from refinery fractions exhibit oxidation rates similar to those present in the crude oils from which they are prepared. A rough correlation between oxidation rate and oxygen content of the organic fraction appears to exist, which is consistent with reported data for pure compounds.

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The geochemistry of some natural acid glasses from the North Atlantic Tertiary volcanic province

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Abstract—This paper deals with the distribution of some trace and major elements in pitchstones from Arran, Eigg and Iceland. The distribution of trace elements in the residual glasses of the porphyritic pitchstones and in a few of the phenocrysts is also considered. Of the trace elements, Mo, Sn, Ni, Co, Cu, Zn, Cd, Pb, S and As have been determined chemically, Rb and Zr by X-ray fluorescence and Ga, Cr, V, Nb, Li, Y, La, Sr and Ba spectrographically. As the pitchstones represent only a limited range of composition, great variation is not found, but the group of Arran pitchstones is shown to be chemically distinct from the Icelandic group.

Introduction

In this paper, the results of a geochemical study of some natural acid glasses (pitchstones and obsidians) from the north Atlantic Tertiary volcanic province are presented. Pitchstones and obsidians are found throughout the province, and are particularly well developed in the Tertiary volcanic sequence of eastern Iceland, where they occur as the chilled margins of high-level acid intrusions, as dykes, and as the chilled envelopes of finely crystalline acid lavas. In Scotland, the island of Arran has long been famous for its pitchstones, dykes and sills, and to the north, the isle of Eigg contains several pitchstones, including the porphyritic sub-acid pitchstone which forms the celebrated Sgurr of Eigg.

These natural acid glasses are possible differentiates of tholeiitic magma, and as such were considered by Nockolds and Allen (1956) as part of their study of the geochemistry of tholeiitic series in general. The new analytical results are presented in the same way as those of Nockolds and Allen, so allowing this data, which is obtained from a suite of rocks of rather restricted composition, to be compared with that of the province as a whole.

The chemical analyses of the porphyritic pitchstones, their residual glasses and the feldspar phenocrysts together with the modes have already been published (Carmichael, 1960a,b) as have the analyses of a group of largely non-porphyritic pitchstones (Carmichael 1961). The modes of many of the pitchstones are given in Tables 4(a), 5(a) and 6(a), and those analyses unaccompanied by modal data contain 1 per cent or less total phenocrysts, which are mainly feldspar.

As the chemical determinations of the trace elements are reasonably precise, all the results given in the tables with the exception of the spectrographic determinations have been recalculated (together with the major elements) on a water-free basis.

The analyses have been plotted against a modified Larsen factor

$$[(\tfrac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$$

so as to correspond with the data presented by Nockolds and Allen (1956). As the pitchstones represent only a limited range of composition, great variation is not to be expected, and accordingly the scale has been considerably expanded over that used by Nockolds and Allen (1956).

The first author is responsible for the major analyses and for the preparation of the samples for all the colorimetrically determined trace elements up to the stage of visual comparison which was done solely by the second author, who also made many of the polarographic determinations. The first author is also responsible for the writing of the paper.

Analytical Methods

The chemical methods for the determination of Cd, Co, Cu, Ni, Pb, Sn and Zn have already been briefly described (Carmichael and McDonald, 1961) and it was concluded in that account that cobalt was incompletely extracted by dithizone in the standard rocks G–1 and W–1, which were included in each batch of samples. It has been found subsequently that an excessive concentration of hydroxylamine in the aqueous solution impedes the extraction of Co by dithizone. The concentration of $NH_2OH.HCl$ has been reduced to a minimum and the results for Co for G–1 and W–1, respectively are, 1·8, 1·8, 2·0, 2·1; average 1·9 p.p.m., and 45, 47, 47, 49; average 47 p.p.m. These new determinations agree reasonably well with the neutron-activation Co results (Ahrens and Fleischer, 1960)(G–1, 2·2; W–1, 51 p.p.m.).

The methods not previously described are those for sulphur, which was determined gravimetrically as $BaSO_4$ after fritting 1 g of powdered sample with Na_2O_2 in a nickel crucible; this method is not particularly accurate in the range 0–200 p.p.m. (Wager *et al.*, 1957, p. 873).

Arsenic was determined after fusion of the rock powder with NaOH in a nickel crucible, the cooled melt being leached with water and filtered into a conical flask. After addition of $SnCl_2$ and KI to the acidified filtrate, metallic zinc was added, and the evolved arsine absorbed in a Gutzeit apparatus. The sample stains were matched visually against standards treated in the same way (Sandell, 1959, pp.289–292). The results for G–1 and W–1 are, respectively 0·8, 0·8, 1·0; average 0·9 p.p.m., and 1·8, 1·9, 2·0; average 1·9 p.p.m. These results agree with the colorimetric results of Onishi and Sandell (1955)(G–1, 1·0; W–1, 1·8 p.p.m.).

Several methods of sample attack were tried for the determination of molybdenum, although in all cases dithiol was used as the colorimetric reagent. Powdered samples (0·5 g) were fused with Na_2CO_3 and Mo subsequently determined by the method described by North (1956). Decomposition of the powdered sample by hydrofluoric acid was also tried, the Mo dithiol complex again being extracted into amyl acetate, and compared visually. This method gave erratic results. Mo was determined in the pitchstones by both methods, but the authors believe that the results obtained are not entirely satisfactory. The two standards G–1 and W–1 were included in each batch and gave the following results; G–1, 6·5, 7·0; W–1, 0·5, 0·5 p.p.m. These results are in agreement with those of Kuroda and Sandell (1954)(G–1, 6·6; W–1, 0·5 p.p.m.).

Cadium was determined polarographically, using a square-wave polarograph, which was also used to determine Cu, Pb and Zn in the ilmenomagnetites.

With the exception of rubidium and zirconium the remaining trace elements were determined spectrographically by Dr. J. R. Butler. The wavelengths of the relevant lines (in Å) which have been used are: Li 6707·84, V 3185·39 and 4379·23, Cr 4254·34, Co 3453·50, Ni 3414·76, Ga 2943·63, Sr 4607·33, Y 3327·87, Mo 3170·34, Nb 2950·87, Ba 4934·08 and La 3245·12. Excitation and electrodes follow the recommendations of Mitchell (1940), and a Hilger quartz prism instrument (E.742) was used throughout. The lines for V, Cr, Co, Ni, Ga, Y, Mo, Nb and La were recorded on Kodak B.10 plates, those of Sr and Ba on Kodak IV.J plates and that of Li on Kodak I.R.E.R. plates.

The standard rock G–1 was used as an external standard, and comparisons with this standard were made visually, with a relative precision of ± 40 per cent.

Rb and Zr were estimated by an X-ray fluorescent method using an ARL Quantometer with a Machlett OEG-60 tube. Two grammes of 100-mesh powdered sample were mixed with 2 g of powdered cellulose and compressed at 16,000 lb/in^2 to form a disk $1\frac{1}{4}$ in diameter. The disk was irradiated with primary X-rays generated at 40 kV and 30 mA, and the intensity of the fluorescent RbK_α and ZrK_α radiations integrated over 300 sec. The standard G–1 was used as an external standard, the determinations having a relative precision of ± 10 per cent.

The elements Co, Mo and Ni were determined chemically and spectrographically and as these

three elements in the samples are near the limits of spectrographic detection, the results quoted in the tables are those derived chemically. The results of the spectrographic determinations, however, were in good agreement with those obtained chemically.

The limit of detection has not been given for any of the chemical methods since it is dependent on initial sample weight and subsequent dilution volumes. In general a 1 g sample was used with fixed dilution factors and no attempt was made to vary these for increased sensitivity if this particular limit was approached. The level of Cd is sometimes rather low, so that with the dilution factor and electrolyte used, the polarograph is near the limit of reliable determination, especially as a reagent blank is always obtained.

The variation attributable to analytical error may be illustrated for the chemical trace-element determinations by the results of the replicate analyses of the standard rocks G–1 and W–1, which were included in each batch of samples. Some of the results for these two standards have been recorded previously (Carmichael and McDonald, 1961) and other results have been noted above. All the chemical trace-element determinations for the pitchstones and residual glasses were made in duplicate or triplicate, and the results showed similar precision to that obtained for G–1 and W–1 (Carmichael and McDonald, 1961). The results for cadmium are, however, more precise than originally reported for G–1 and W–1 (Carmichael and McDonald, 1961) as the original polarographic standard addition technique was changed to a more precise calibration method.

Mineral Analyses

Phenocrysts of feldspar, iron-rich pyroxene and olivine may occur in many of the pitchstones from Arran, Eigg and Iceland, together with microphenocrysts of ilmenomagnetite. Unfortunately the phenocrysts are not abundant [cf. modal analyses, Tables 4(a), 5(a) and 6(a)] and only a few of the feldspar phenocrysts and the ilmenomagnetites were available for analysis.

The distribution of trace elements in minerals is perhaps best considered in terms of the distribution factor. This term was introduced into petrology by Wager and Mitchell (1951) and relates the concentration of an element in a solid phase to the concentration of that element in the liquid phase (residual glass), the two phases being in equilibrium. The great value of distribution factors is that they "emphasize the importance of the concentration of the trace element in the liquid in controlling the amount of the trace element in the crystal phases separating" (Wager and Mitchell, 1951, p. 166).

The limitations of the mutual replacement (diadochy) of ions in magmatic minerals provided by Goldschmidt's Rules (1937) and by Ringwood's (1955a) modifications allow predictions to be made of the substitutions likely to be found in magmatic minerals. The extent to which these substitutions may occur in natural magmas is not predictable and may be controlled by the concentration of the trace element in the liquid, so that the distribution factor, which makes allowance for the concentration in the liquid, illustrates the relative ease of entry of a trace element into the structure of a solid phase.

Feldspar Phenocrysts

The distribution factors of the analysed feldspar phenocrysts, together with the analytical data is given in Tables 1 and 2. There are no data obtained from rocks of similar composition for comparison, so that the distribution factors of the latest of the Skaergaard gabbros (fayalite ferrogabbro) have been used wherever possible (Wager and Mitchell, 1951, Table 6).

Table 1. Analyses of feldspar phenocrysts
(trace-elements in p.p.m.)

	r	(1)	(2)	(3)
Si^{4+}	0·42	297 × 10^3	306 × 10^3	302 × 10^3
Al^{3+}	0·51	113 × 10^3	108 × 10^3	107 × 10^3
Fe^{3+}	0·64	3 × 10^3	4 × 10^3	3 × 10^3
Na^{1+}	0·97	68 × 10^3	67 × 10^3	45 × 10^3
Ca^{2+}	0·99	24 × 10^3	16 × 10^3	9 × 10^3
K^{1+}	1·33	8 × 10^3	17 × 10^3	59 × 10^3
Composition (wt. per cent)		$Or_5Ab_{78}An_{17}$	$Or_{12}Ab_{77}An_{11}$	$Or_{42}Ab_{52}An_6$
Li^{1+}	0·68	5	10	10
Ni^{2+}	0·69	0·8	0·8	0·5
Co^{2+}	0·72	*	*	*
Cu^{2+}	0·72	7	5	3
Zn^{2+}	0·74	26	18	7·5
Cd^{2+}	0·97	—	0·09	0·08
Sr^{2+}	1·12	300	400	180
Pb^{2+}	1·20	8	7·5	14
Ba^{2+}	1·34	1000	>2000	>2000

Key to Analyses

(1) Feldspar phenocrysts from no. 12, Table 4(b) (anal. 8F, Carmichael, 1960b).
(2) Feldspar phenocrysts from no. 3, Table 4(b) (anal. 7F, Carmichael, 1960b).
(3) Feldspar phenocrysts from no. 3, Table 6(b) (anal. 1F, Carmichael, 1960b).

*Below the limit of sensivity (0.2 p.p.m. Co).

In this and succeeding tables, r refers to the ionic radius given by Ahrens (1952) for the valency indicated.

Table 2. Feldspar distribution factors
(phenocryst/liquid)

	(1)	(2)	(3)	Sk.
Fe*	0·2	0·1	0·2	—
Li	0·8	1·7	0·4	<0·06
Ni	1·1	1·1	2·2	—
Cu	0·8	0·8	1·0	0·03†
Zn	0·3	0·1	0·1	—
Na	2·1	2·2	1·3	—
Cd	—	0·4	0·6	—
Ca	4·8	1·5	1·3	—
Sr	6·7	3·2	4·0	5·0
Pb	1·6	1·2	1·2	—
K	0·3	0·4	1·2	—
Ba	0·8	>1·5	>2·2	1·0

Key to Analyses

(1) Feldspar phenocrysts (Table 1, no. 1) and residual glass (Table 4(b), no. 12G).
(2) Feldspar phenocrysts (Table 1, no. 2) and residual glass (Table 4(b), no. 3G).
(3) Feldspar phenocrysts (Table 1, no. 3) and residual glass (Table 6(b), no. 3G).

Sk., Skaergaard fayalite ferrogabbro plagioclase distribution factors (Wager and Mitchell, 1951, Table 6).

* Distribution factor calculated from $Fe^{2+} + Fe^{3+}$ in liquid and Fe^{3+} in feldspars.

† Immiscible sulphide phase not taken into account in estimating Cu in liquid (Wager and Mitchell, 1951, p. 149).

The only trace element that shows considerable enrichment in the feldspars compared to the liquids is Sr, the degree of enrichment being comparable to that of the plagioclase of the Skaergaard ferrogabbros (Table 2). The level of Sr in these feldspars (180–400 p.p.m.) is very much lower than that of the more calcic Skaergaard plagioclase (2000 p.p.m.). It is of interest that the distribution factors for Sr are higher than those of Ca, indicating the greater ease of entry of Sr compared to Ca. Similar behaviour was noted in the Skaergaard plagioclases (Wager and Mitchell, 1951, p. 149) and commented on by Ringwood (1955a, p. 194).

Lead shows slight enrichment in the feldspars compared to the liquids, and is also enriched relative to K, the distribution factor for Pb being greater than or equal to that for K. Although this behaviour is to be expected on the basis of ionic radii (Pb^{2+}, 1·20 Å; K^{+}, 1·33 Å) and larger charge, it is not in accordance with the electronegativities (Ringwood, 1955a, p. 196). Barium is also slightly enriched in the feldspars compared to the liquids, the degree of enrichment becoming greater with the increase of the smaller K distribution factor. The feldspars are impoverished in Cd, the distribution factors being less than unity, and although Cd^{2+}(0·97 Å) has a similar radius to Ca^{2+}(0·99 Å), Vincent and Bilefield (1960) have shown that there is a complete lack of geochemical coherence between Ca and Cd. The two feldspars contain less Cd than a Skaergaard plagioclase (0·15 p.p.m. Cd, Vincent and Bilefield) although the distribution factors may be similar as the Skaergaard liquids generally contain more Cd.

Copper may exist in two valency states, and Cu^{+} (0·96 Å) may be camouflaged by Na^{+} (0.97 Å) whereas Cu^{2+} (0.72 Å) will be camouflaged by Fe^{2+} (0.74 Å). If Cu in the feldspars is univalent then the distribution factor of Cu compared to that of Na indicates that Na has greater ease of entry, although if Cu is divalent then the distribution factors of Cu and Fe indicate that Cu is accepted in the feldspars with greater ease. The distribution factor of Fe in the feldspars is computed from the total iron in the residual glasses, for although divalent iron has not been found in these feldspars, it probably exists, and will camouflage Cu as well as Ni and Zn.

The distribution of Ni compared to that of iron indicates that Ni is preferentially accepted and it may also show slight enrichment relative to the liquid, whereas Zn is impoverished in the feldspars compared to the liquids. It is perhaps coincidence that the level of Zn declines with the anorthite (calcium) content of the feldspar; this, however, may generally be expected if the distribution factor remains constant, as Zn tends to be concentrated in basic rocks. The feldspar analyses presented by Wedepohl (1953) have similar contents of Zn, and also show a decrease in the concentration of Zn as the anorthite content decreases.

Lithium is present in the feldspar phenocrysts and although both Wager and Mitchell (1951, p. 147) and Sen *et al.* (1959, p. 61) have suggested that Li in feldspars may be the result of subsequent alteration, these feldspars appear quite fresh, and are believed to hold Li in their structure.

Ilmenomagnetite Microphenocrysts

Only partial analyses have been made of some of the ilmenomagnetite microphenocrysts (Table 3) and as only small quantities (50 mg) were available, the analytical results do not have the precision of the pitchstone analyses. The elements

Ni, Co, Cu, Zn and Mn which are the only ones so far determined, may all be camouflaged by divalent iron.

The distribution factors show considerable variation and indicate that all the iron ores are greatly enriched in the elements Ni, Co, Cu, Zn and Mn compared to their liquids. The concentration of Ni in these iron ores is very much higher than in the magnetite of the Skaergaard fayalite ferrogabbros (Wager and Mitchell, 1951, Table B) where Ni is less than 2 p.p.m., whereas, in contrast, Co is similar, there being 3 p.p.m. in the Skaergaard iron ore (Wager and Mitchell, 1951, Table B)

Table 3. Partial analyses of ilmeno-magnetite microphenocrysts (values in p.p.m.)

	r	(1)	(2)	(3)	(4)	(5)	(6)
Ni^{2+}	0·69	15	50	20	25	15	15
Co^{2+}	0·72	5	5	5	5	20	15
Cu^{2+}	0·72	30	30	70	80	75	40
Zn^{2+}	0·74	1400	1800	2200	1300	1100	900
Mn^{2+}	0·80	13,000	15,300	6700	5100	5400	9300
Pb was below the limit of sensitivity (20 p.p.m.)							

Distribution factors (phenocryst/liquid)

	(1)	(2)	(3)	(4)	(5)	(6)
Ni	21	70	29	36	15	75
Co	17	17	—	17	—	75
Cu	5	3	8	13	19	13
Zn	7	12	23	17	22	11
Mn	8	22	17	17	27	12

Key to Analyses

(1) Separated from no. 3 (Table 4b).
(2) Separated from no. 9 (Table 4b).
(3) Separated from no. 12 (Table 4b).
(4) Separated from no. 1 (Table 5b).
(5) Separated from no. 5 (Table 5b).
(6) Separated from no. 3 (Table 6b).

and between 5 and 20 p.p.m. in these. The Skaergaard fayalite ferrogabbro magnetites have very much higher Cu (200–300 p.p.m.) (Vincent and Phillips, 1954, Table 2) than these micro-phenocrysts (30–80 p.p.m.), whereas the level of Zn is comparable, these ilmenomagnetites containing between 900 and 2200 p.p.m. Zn and the Skaergaard magnetites 1700 and 650 p.p.m. (Vincent and Phillips, 1954, Table 2).

Major and Trace Elements in the Pitchstones and Residual Glasses

Nockolds and Allen (1956) have recognised three trends in the British Tertiary tholeiitic series; an iron-rich trend which is particularly well developed in Iceland and which is characterized by absolute enrichment in iron; a British main trend with slight absolute enrichment in iron and a third British trend with no absolute enrichment in iron.

For each of these three trends the variation between Ca, Na and K may also be shown, and NOCKOLDS and ALLEN (1956, Figs. 36 to 38) have indicated that the iron-rich trend is matched by enrichment of Na relative to K, particularly in the acid members along the supposed liquid line of descent. The main trend and the third trend each show correspondingly less enrichment of Na to K, and the variation curves are accordingly displaced towards the K corner.

Variation diagrams showing the relation between $(Fe^{2+} + Fe^{3+})$, Mg and (Na + K), and between Ca, Na and K for the British (Arran and Eigg) and Icelandic

Fig. 1. Variation diagram of the Icelandic pitchstones. Solid circles (pitchstones) and open circles (residual glasses) refer to variation in $(Fe^{2+} + Fe^{3+})$, Mg and (Na + K); crosses refer to Ca, Na and K, with the arrows on the tielines indicating the position of the residual glasses.

pitchstones are given in Figs. 1 and 2. The Arran pitchstones tend to cluster nearer the K corner than the Icelandic pitchstones, but there is no appreciable distinction with respect to $(Fe^{2+} + Fe^{3+})$, Mg and (Na + K). It would appear then, as NOCKOLDS and ALLEN (1956) suggest, that the factors which control the degree of iron enrichment in the associated Icelandic basalts and andesites also exert an influence on the variation of Na and K, so that the Icelandic pitchstones are characteristically richer in Na relative to K compared to the Arran pitchstones. In some of the Icelandic pitchstones this relative enrichment has been augmented by a subsequent hydrothermal alteration, one of the effects of which is to decrease the K content (CARMICHAEL, 1961). As this alteration is progressive it is difficult to decide

which pitchstones are completely unaltered, but the same order of enrichment of Na relative to K may be seen in a completely fresh post-glacial obsidian (Table 4, no. 7) and in unaltered crystalline rhyolites (unpublished analyses).

In view of the small amount of data on the distribution of trace elements in the phenocrysts of these porphyritic pitchstones, the residual glasses of ten porphyritic natural acid glasses have been separated and analysed. The analyses of the residual glasses taken in conjunction with their respective pitchstones indicates whether the total phenocrysts are enriched in relation to the liquid (glass) or

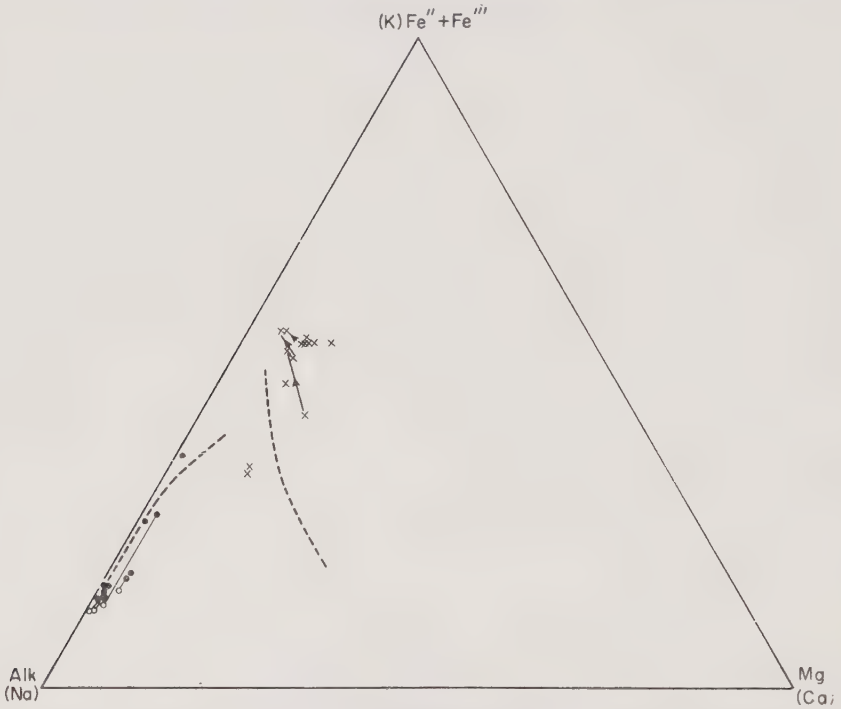


Fig. 2. Variation diagram of the British pitchstones. Dashed line represents the Icelandic trend.

impoverished in a particular element. The trend of the tie-lines between the pitchstones and their residual glasses (Figs. 3 to 7) illustrates the behaviour to be expected in rocks derived from a parental liquid by the separation of early-formed crystals.

The data of the major and trace elements of the pitchstones and their residual glasses is given in Tables 4, 5 and 6 and the variation with respect to the modified Larsen factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ (cf. Nockolds and Allen, 1956) in Figs. 3 to 8. Two of the Arran pitchstones (Table 5, nos. 1 and 5) contain xenocrysts of quartz (Carmichael 1961), and the former (no. 1) also contains orthopyroxene xenocrysts. These xenocrysts will tend to give an aberrant value of the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$, as will the Icelandic hydrothermal alteration (noted above), the effects of which are particularly noticeable in nos. 1, 2, 4, and 5 (Table 4b).

Silicon (Figs. 3*a*, 3*b*)

The residual glasses of the Icelandic porphyritic pitchstones are all enriched in Si compared to their pitchstones, the total phenocrysts being impoverished in Si. The

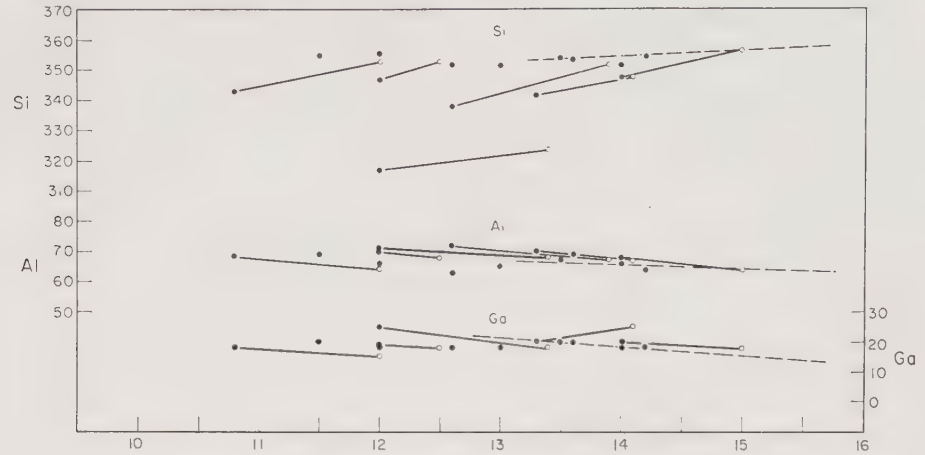


Fig. 3(a). The Icelandic pitchstones. The dashed lines represent the British trend for each element (Fig. 3b).

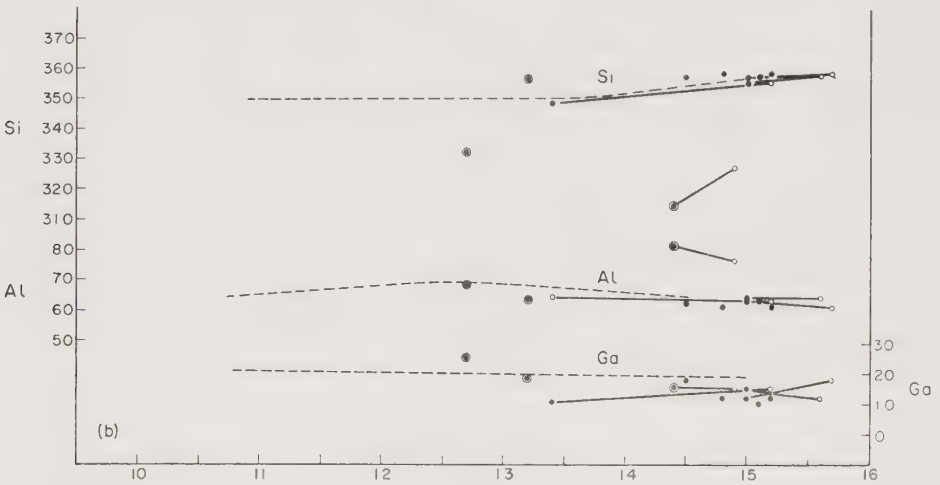


Fig. 3(b). The Arran and Eigg pitchstones. The three Eigg pitchstones are represented by solid circles in open circles. The dashed lines represent the Icelandic trend for each element (Fig. 3a).

Figs. 3(a) and 3(b). Variation in silicon, aluminium and gallium (in p.p.m.). Pitchstones (solid circles) are joined to their respective residual glasses (open circles).

residual glasses and the non-porphyritic pitchstones all lie on a smooth line, whereas the porphyritic pitchstones are displaced from this trend, so that the variation of Si with the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ for rocks which owe their origin to the separation of the early-formed crystals is likely to show some scatter, and will not lie on a smooth line.

The Arran pitchstones and their residual glasses show little variation in Si.

whereas two of the Eigg pitchstones are less rich in Si, with one of them (Table 6, no. 3) being completely off the general trend.

Aluminium and gallium (Figs. 3*a*, 3*b*)

The similarity of the ionic radius of Ga^{3+} (0·62 Å) to the ionic radius of Al^{3+} (0·51 Å) and Fe^{3+} (0·64 Å) indicates that Ga is likely to be found in feldspars and magnetites (Wager and Mitchell, 1951; Wilkinson, 1959), and as feldspars are normally more abundant, they will make the dominant contribution of Ga to an igneous rock. Accordingly the variation of Ga in this suite of rocks is shown with respect to Al.

The Icelandic residual glasses all have lower Al than their pitchstones, the phenocrysts (predominantly feldspar) being enriched relative to the liquid. The Icelandic Al curve possibly passes through a weak maximum as the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases.

The Arran residual glasses have the same or slightly less Al than their pitchstones, for if feldspar phenocrysts are abundant, they are accompanied by quartz which tends to minimize the contribution of Al by the feldspar. The sub-acid Eigg pitchstone contains abundant feldspar phenocrysts and shows a correspondingly large decrease in Al in its residual glass (Table 6, no. 3).

Ga generally decreases in the Icelandic residual glasses compared to their pitchstones but for the Icelandic pitchstones as a group it remains approximately constant with increase in the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$. The Ga concentration of the Arran residual glasses does not behave consistently with respect to their pitchstones and the general curve of Ga variation for Arran and Eigg declines slightly with increase in the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$. The Arran pitchstones show little variation in Ga, and the decline in the Ga curve is due to higher Ga in two Eigg pitchstones. The Icelandic Ga curve is slightly higher than that for Arran, the average concentrations being 19 and 13 p.p.m., respectively. The Icelandic pitchstones also show greater enrichment of Ga with respect to Al, the average ratio $\text{Ga} \times 1000/\text{Al}$ being 0·29 compared to 0·20 for Arran. There does not seem to be any consistent variation of this ratio in the residual glasses compared to their pitchstones.

Lithium and magnesium (Figs. 4*a*, 4*b*)

The phenocrysts of the Icelandic porphyritic pitchstones are enriched in Li and Mg compared to the liquids (residual glass), but there is a considerable range of values for Li in this group of pitchstones, and no significant variation as the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, in contrast to Mg which decreases steadily. The same features are shown in the Arran pitchstones and their residual glasses, which are also impoverished in Li and Mg compared to the phenocrysts. As Li tends to be concentrated in acid rocks (Goldschmidt, 1954), the relative enrichment of the phenocrysts in Li suggests that it shows a maximum in passing from basic to acid rocks, especially if the acid liquids owe their origin to the separation of early-formed crystals from a parental liquid. A weak maximum for Li was noted in the Skaergaard liquids (Wager and Mitchell, 1951, Table 10) where the fifth liquid contains more Li than either the fourth or the sixth liquids.

The Li curve for the Arran pitchstones is considerably higher than the Icelandic curve and the average of seven Arran pitchstones (24 p.p.m.) correspondingly higher than the Icelandic average (11 p.p.m.), but the wide range of values of the Icelandic samples invalidates any conclusion of a regional variation.

Chromium, vanadium, iron, manganese and titanium (Figs. 4*a*, 4*b*)

The residual glasses of the Arran and Icelandic pitchstones are impoverished in Cr, V, Fe, Mn and Ti compared to their phenocrysts, although V is occasionally

Table 4(a). Modal analyses of Icelandic pitchstones (vol. per cent)

	Glass	Feldspar	Pyroxene	Olivine	Iron oxides	Basaltic xenoliths
1	94·3	2·5	0·3	—	0·1	2·8
2	97·6	2·2	<0·1	0·2	—	—
3	86·7	9·2	0·5	—	0·2	3·4
4	96·1	3·4	0·2	0·2	0·1	—
6	89·0	8·1	1·6	0·7	0·6	—
9	92·0	6·0	0·4	—	0·4	1·2
11	98·0	2·0	—	—	—	—
12	89·6	8·9	0·8	0·2	0·3	0·2

Nos. 5, 7, 8, 10, 13 and 14 contain 1 per cent or less total phenocrysts.

enriched in the residual glasses. Cr frequently falls below the limit of sensitivity in all the pitchstones, and little variation with increase in the factor

$$[(\tfrac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$$

may be seen. V tends to decrease slightly in the Icelandic pitchstones with increase in the factor, whereas in the British pitchstones it remains constant. Mn and Ti show a small decrease in both the Icelandic and Arran pitchstones as the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ increases, the Icelandic pitchstones having a higher concentration of Mn than those from Arran, whereas Ti is similar in both groups. The Eigg pitchstones are all higher in Mn and Ti than the Arran specimens.

The phenocrysts of all the porphyritic pitchstones are enriched in Fe compared to the liquids, and both the British and Icelandic pitchstones decrease in Fe as the factor

$$[(\tfrac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$$

increases, the Icelandic group being generally richer in Fe than those from Arran.

Niobium (Figs. 4*a*, 4*b*)

The similarity of the ionic radius of Nb^{5+} (0·69 Å) to that of Ti^{4+} (0·68 Å) indicates that Nb is likely to be found in Ti minerals (Goldschmidt, 1954). Nb is in fact concentrated in residual magmas which is contrary to the behaviour to be expected by its higher charge, and this anomaly has been explained by (Ringwood, 1955b) the tendency of Nb to form complexes in silicate liquids.

Table (4b). Icelandic pitchstones

	r	(1)	(1G)	(2)	(3)	(3G)	(4)	(4G)	(5)	(6)
Si^{4+}	0·42	343×10^3	353×10^3	355×10^3	317×10^3	328×10^3	347×10^3	353×10^3	356×10^3	338×10^3
Al^{3+}	0·51	68×10^3	64×10^3	69×10^3	71×10^3	68×10^3	70×10^3	68×10^3	66×10^3	72×10^3
Ti^{4+}	0·68	3×10^3	2×10^3	1×10^3	4×10^3	3×10^3	2×10^3	1×10^3	1×10^3	2×10^3
Fe^{3+}	0·64	16×10^3	9×10^3	8×10^3	12×10^3	9×10^3	7×10^3	5×10^3	6×10^3	5×10^3
Mg^{2+}	0·66	4×10^3	2×10^3	1×10^3	4×10^3	2×10^3	1×10^3	1×10^3	1×10^3	1×10^3
Fe^{2+}	0·74	12×10^3	16×10^3	7×10^3	31×10^3	32×10^3	14×10^3	12×10^3	10×10^3	20×10^3
Na^{1+}	0·97	32×10^3	33×10^3	29×10^3	38×10^3	30×10^3	38×10^3	40×10^3	32×10^3	37×10^3
Ca^{2+}	0·99	16×10^3	13×10^3	18×10^3	14×10^3	11×10^3	14×10^3	10×10^3	16×10^3	13×10^3
K^{1+}	1·33	14×10^3	17×10^3	16×10^3	32×10^3	38×10^3	18×10^3	18×10^3	18×10^3	27×10^3
P^{5+}	0·35	400	300	100	500	500	100	200	200	300
Ga^{3+}	0·62	18	15	20	25	18	18	18	18	—
Cr^{3+}	0·63	7	*	*	*	*	2	*	*	—
V^{3+}	0·74	20	15	15	20	15	10	12	15	—
Nb^{5+}	0·69	25	30	40	25	30	20	30	20	—
Mo^{4+}	0·70	1·3	—	2·6	2·9	—	2·4	2·5	3·0	2·9
Sn^{4+}	0·71	—	—	4·5	4·0	—	3·4	—	2·0	1·6
Li^{1+}	0·68	6	*	4	20	6	*	*	*	—
Ni^{2+}	0·69	2·3	2·6	0·2	0·5	0·7	0·7	0·1	0·9	0·9
Co^{2+}	0·72	4·0	0·9	*	1·1	0·3	0·4	*	0·9	2·1
Cu^{2+}	0·72	14	13	13	5	6	8	9	8	9
Zn^{2+}	0·74	106	80	150	185	200	125	115	155	105
Zr^{4+}	0·79	570	600	390	650	825	400	340	410	—
Mn^{2+}	0·80	1000	900	500	1700	1600	800	600	300	600
Y^{3+}	0·92	40	50	40	60	40	40	40	40	—
Cd^{2+}	0·97	0·11	0·10	0·29	0·25	0·24	0·21	0·22	0·20	0·19
La^{3+}	1·14	150	110	210	150	120	75	110	110	—
Sr^{2+}	1·12	125	125	200	180	125	180	125	60	—
Pb^{2+}	1·20	9	5	6	10	6	6	5	11	10
Ba^{2+}	1·34	1300	1300	1800	1300	1300	900	1300	750	—
Rb^{1+}	1·47	110	170	130	100	120	90	90	120	—
S		290	—	250	360	—	—	—	130	210
As		0·5	—	1·2	1·3	—	1·2	—	1·3	3·3
Fe		88	93	94	92	95	95	95	94	96
Mg		12	7	6	8	5	5	5	6	4
Fe		36	32	25	37	37	27	22	24	28
Mg		5	3	1	3	2	1	2	1	1
Alk		59	65	74	60	61	72	76	75	71
Position		10·8	12·0	11·5	12·0	13·4	12·0	12·5	12·0	12·6

All the Icelandic residual glasses are enriched in Nb compared to their phenocrysts, and in the Icelandic group as a whole, Nb increases with increase in the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$. The British (Arran and Eigg) pitchstones show no variation as the factor increases nor are the residual glasses enriched in Nb.

The average concentration of Nb in the Icelandic pitchstones (26 p.p.m.) is higher than that of the Arran pitchstones (17 p.p.m.) and the Nb/Zr ratio in both series (Iceland, 1:15; Arran, 1:14) is close to the 1:10 ratio found by Goldschmidt (1954) who noticed that in igneous rocks the concentration of Nb followed that of Zr.

Molybdenum (Figs. 4*a*, 4*b*)

In a detailed survey of the geochemistry of Mo, Kuroda and Sandell (1954) show that Mo tends to be concentrated in granitic rocks although there is no ready correlation between it and a major element.

Table 4(*b*) (*contd.*)

(6G)	(7)	(8)	(9)	(9G)	(10)	(11)	(12)	(12G)	(13)	(14)
352×10^3	352×10^3	352×10^3	342×10^3	348×10^3	354×10^3	354×10^3	348×10^3	357×10^3	352×10^3	355×10^3
67×10^3	63×10^3	65×10^3	70×10^3	67×10^3	67×10^3	69×10^3	68×10^3	64×10^3	66×10^3	64×10^3
1×10^3	2×10^3	1×10^3	2×10^3	1×10^3	1×10^3	1×10^3	2×10^3	1×10^3	1×10^3	1×10^3
3×10^3	5×10^3	8×10^3	8×10^3	6×10^3	6×10^3	6×10^3	6×10^3	4×10^3	6×10^3	4×10^3
1×10^3	1×10^3	2×10^3	2×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3
11×10^3	20×10^3	12×10^3	14×10^3	14×10^3	11×10^3	5×10^3	11×10^3	8×10^3	9×10^3	11×10^3
38×10^3	32×10^3	35×10^3	40×10^3	38×10^3	35×10^3	30×10^3	35×10^3	32×10^3	38×10^3	35×10^3
7×10^3	12×10^3	9×10^3	7×10^3	4×10^3	7×10^3	11×10^3	7×10^3	5×10^3	6×10^3	7×10^3
30×10^3	22×10^3	24×10^3	28×10^3	30×10^3	25×10^3	30×10^3	32×10^3	36×10^3	30×10^3	32×10^3
200	100	200	200	100	100	100	100	200	200	100
—	18	18	20	25	20	20	20	18	18	18
—	30	*	4	*	3	*	4	*	3	3
—	15	12	20	15	15	15	12	10	10	12
—	20	25	30	40	20	30	30	35	30	30
3·0	2·2	2·7	3·0	3·1	3·4	2·1	2·4	—	2·1	2·3
—	3·0	3·2	1·6	—	3·7	—	1·7	—	0·8	1·6
—	30	12	9	4	3	3	9	6	25	25
1·3	0·8	0·2	0·9	0·7	0·2	0·6	0·4	0·7	0·8	0·4
*	2·0	0·3	1·3	0·3	1·4	2·7	1·0	*	0·3	0·6
7	12	9	11	9	6	8	9	9	9	7
80	122	115	152	148	95	135	100	95	115	90
—	435	130	620	580	350	320	360	250	330	310
400	800	600	800	700	500	300	500	400	500	500
—	40	40	60	60	40	40	40	40	70	40
0·15	0·14	0·20	0·23	0·25	0·15	0·19	0·23	0·24	0·17	0·17
-	110	190	150	150	200	150	150	110	400	110
—	180	75	125	45	60	125	90	45	60	90
6	7	10	10	6	11	15	9	5	9	9
—	1000	900	900	1000	900	900	1000	1300	900	1300
—	70	150	125	125	95	175	100	105	90	105
--	100	190	150	—	85	165	140	—	120	75
—	1·4	1·9	2·1	—	1·5	1·8	1·0	—	0·7	1·8
94	96	91	92	95	94	92	95	92	94	94
6	4	9	8	5	6	8	5	8	6	6
17	31	25	24	23	22	15	20	15	18	18
1	1	2	2	1	1	1	1	1	1	1
82	68	73	74	76	77	84	79	84	81	81
13·9	12·6	13·0	13·3	14·1	13·5	13·6	14·0	15·0	14·0	14·2

An asterisk indicates that the element is below the limit of sensitivity which for Cr is (1) and for Li (1) p.p.m. The limit for the chemical determinations of Co are 0·2 p.p.m.
A dash indicates that the sample was not analysed.
Position refers to the value of the factor $[(\frac{1}{3}\,\mathrm{Si} + \mathrm{K}(- (\mathrm{Ca} + \mathrm{Mg})]$
For the key to the analyses see p. 220.

It is not considered that the Icelandic or Arran residual glasses show any significant variation in Mo compared to their phenocrysts, but the Eigg residual glass may show slight enrichment.

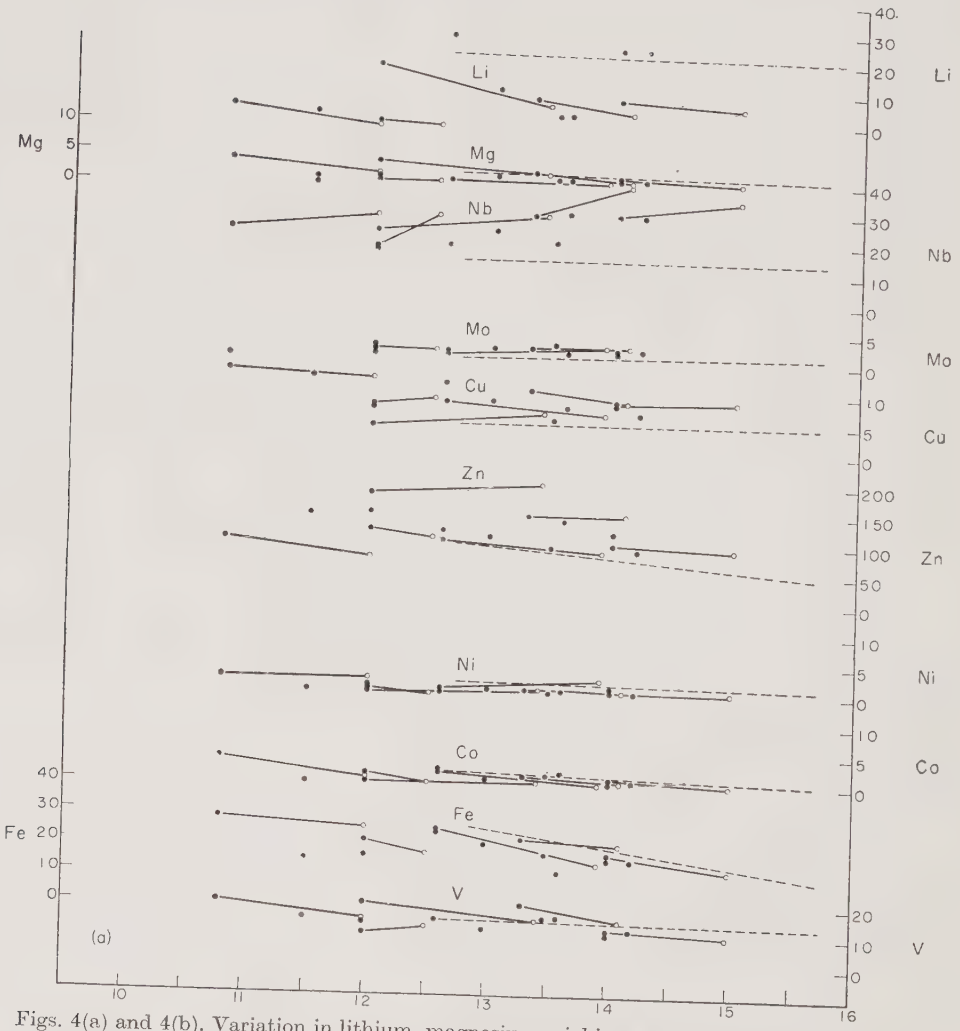
There is no variation in Mo as the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ increases over the limited range of composition represented here for either the British or the Icelandic samples, but the level of Mo in the Icelandic pitchstones is higher than those of Arran and the averages are set down below in Table 7 together with comparative data from the literature.

Although the difference in the average level of Mo in the Arran and Icelandic pitchstones indicates a regional variation, there must also be considerable variation

Table 5(a). Modal analyses of Arran pitchstones (vol. per cent).

	Glass	Feldspar	Quartz	Pyroxene	Olivine	Iron oxides
1	83·4	9·4	4·8	1·5	0·6	0·3
2	93·3	4·3	2·3	—	<0·1	—
3	94·6	2·8	2·5	—	0·1	—
4	97·1	2·5	—*	0·2	—	0·2
5	95·3	2·9	1·5	0·1	0·1	0·1

Nos. 6 and 7 have less than 1 per cent total phenocrysts.
* Quartz has subsequently been found in this specimen (approx. 0·2 per cent).



Figs. 4(a) and 4(b). Variation in lithium, magnesium, niobium, molybdenum, copper, zinc, nickel, cobalt, iron and vanadium. Values for Li, Nb, Mo, Co, Zn, Ni, Co and V in p.p.m. Pitchstones (solid circles) are joined to their respective residual glasses (open circles).
Fig. 4(a). The Icelandic pitchstones. The dashed lines represent the British trend for each element (Fig. 4b).

Table 5(b). Arran pitchstones

	r	(1)	(1G)	(2)	(3)	(4)	(4G)	(5)	(5G)	(6)	(7)
Si^{4+}	0·42	349×10^3	356×10^3	358×10^3	359×10^3	356×10^3	358×10^3	358×10^3	359×10^3	358×10^3	359×10^3
Al^{3+}	0·51	65×10^3	64×10^3	63×10^3	62×10^3	65×10^3	65×10^3	64×10^3	62×10^3	64×10^3	62×10^3
Ti^{4+}	0·68	3×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3
Fe^{3+}	0·64	4×10^3	3×10^3	3×10^3	5×10^3	4×10^3	3×10^3	3×10^3	2×10^3	3×10^3	4×10^3
Mg^{2+}	0·66	2×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3	1×10^3
Fe^{2+}	0·74	19×10^3	8×10^3	9×10^3	7×10^3	7×10^3	7×10^3	8×10^3	8×10^3	8×10^3	8×10^3
Na^{+}	0·97	31×10^3	31×10^3	31×10^3	25×10^3	31×10^3	30×10^3	28×10^3	30×10^3	29×10^3	29×10^3
Ca^{2+}	0·99	10×10^3	5×10^3	6×10^3	9×10^3	6×10^3	4×10^3	6×10^3	4×10^3	6×10^3	6×10^3
K^{+}	1·33	30×10^3	39×10^3	33×10^3	38×10^3	38×10^3	42×10^3	38×10^3	41×10^3	39×10^3	39×10^3
P^{5+}	0·35	200	100	100	100	100	100	100	100	100	100
Ga^{3+}	0·62	10	15	18	12	15	12	12	18	10	12
Cr^{3+}	0·63	3	3	5	5	*	*	*	*	4	4
V^{3+}	0·74	10	15	15	10	10	10	10	10	10	10
Nb^{5+}	0·69	15	15	15	30	15	15	15	15	15	15
Mo^{4+}	0·70	1·2	1·2	1·6	1·4	1·6	—	1·9	1·7	1·9	1·6
Sn^{4+}	0·71	1·8	—	1·3	1·1	1·0	—	1·6	—	0·2	1·5
Li^{+}	0·68	25	20	20	4	35	20	35	20	30	20
Ni^{2+}	0·69	1·6	0·7	0·8	1·0	1·6	0·8	1·3	1·0	0·6	0·7
Co^{2+}	0·72	2·1	0·3	1·0	1·7	1·0	*	0·3	*	2·1	1·3
Cu^{2+}	0·72	6	6	5	2	4	5	4	5	7	5
Zn^{2+}	0·74	75	54	39	34	54	45	55	50	50	55
Zr^{4+}	0·79	290	200	250	205	215	190	220	205	220	205
Mn^{2+}	0·80	500	200	300	200	300	200	300	200	300	200
Y^{3+}	0·92	30	40	40	40	30	30	40	40	20	25
Cd^{2+}	0·97	0·10	0·14	0·05	0·05	0·05	0·05	0·12	0·13	0·14	0·06
La^{3+}	1·14	110	120	110	120	110	90	200	150	110	75
Sr^{2+}	1·12	125	60	90	125	75	45	75	45	60	45
Pb^{2+}	1·20	17	13	18	23	17	18	15	12	17	16
Ba^{2+}	1·34	1500	1300	1800	1000	1800	1300	1800	1000	1500	1300
Rb^{+}	1·47	130	170	160	150	170	175	160	170	170	160
S		230	—	150	170	130	—	85	—	180	170
As		2·2	—	1·5	1·2	2·3	—	1·9	—	1·5	2·0
Fe		92	92	92	92	92	91	92	91	92	92
Mg		8	8	8	8	8	9	8	9	8	8
Fe		27	13	16	16	14	12	14	12	14	15
Mg		2	2	1	1	1	1	1	1	1	1
Alk		71	85	83	83	85	87	85	88	85	84
Position		13·4	15·2	14·5	14·8	15·0	15·6	15·0	15·7	15·1	15·2

An asterisk indicates that the element is below the limit of sensitivity which for Cr is (1) and for Li (1) p.p.m. The limit for the chemical determinations of Co is 0·2 p.p.m.
A dash indicates that the sample was not analysed.
Position refers to the value of the factor $[(\frac{1}{3}Si + K) - (Ca + Mg)]$
For the key to the analyses see p. 221.

within the British acid magma as Patterson (1951) reports 7 and 10 p.p.m. Mo in a rhyolite and obsidian from Tardree, Antrim, while a third rhyolite has less than 1 p.p.m. Mo. Although Kuroda and Sandell (1954) found that there was some evidence of regional variation, there was a general uniformity, and slightly less than 10 per cent of their 150 samples of all igneous rocks fell outside the limits 0·2–2 p.p.m. Mo.

Tin

The geochemistry of Sn is not well known, and its concentration in igneous rocks, particularly granites, is believed to be considerably affected by regional variation (Goldschmidt, 1954), although Onishi and Sandell (1957) provide data which shows comparatively little variation of Sn in the granites of north America and Japan.

Goldschmidt (1954), Ringwood (1955) and Onishi and Sandell (1957) all suggest that the content of Sn in igneous rocks increases with the concentration of Si. The few determinations of tin which have been made on the Icelandic and British pitchstones show little consistent variation as the factor

$$[(\tfrac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$$

increases; these pitchstones, however, represent only a limited range of composition. The average concentration of Sn in the Arran pitchstones (1·2 p.p.m.) is lower than that of the Icelandic group (2·6 p.p.m.) and is taken to indicate a small regional variation, although both groups are near the average (3 p.p.m.) of eighty granitic rocks analysed by Onishi and Sandell (1957).

These averages suggest that the Goldschmidt (1954) average of 80 p.p.m. Sn for granitic rocks is unusually high. As Sn has not been determined in any of the constituent minerals (phenocrysts), nothing is known of its distribution within the pitchstones.

Nickel (*Figs.* 4*a*, 4*b*)

Ni^{2+} (0·69 Å) is found in magnesian minerals (Mg^{2+}, 0·66 Å) and hence in magnesian rocks, but the geochemical behaviour of Ni shows not so much camouflage by Mg but high relative enrichment to Fe^{2+} (0·74 Å) (Ringwood, 1955a).

Ni has an unusual distribution in the Skaergaard liquids, for after being almost completely eliminated in the intermediate liquids, it becomes concentrated again in the late acid granophyres (Wager and Mitchell, 1951, Table 10). Perhaps this concentration of Ni in the late liquids is matched by four Icelandic residual glasses which also show enrichment of Ni compared to their phenocrysts. The remaining Icelandic and Arran residual glasses are more normally impoverished in Ni, and in both groups of pitchstones Ni shows a slight decrease as the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ increases, the Icelandic curve lying slightly below the Arran curve and the average being correspondingly smaller (Table 8).

Both groups of pitchstones have less Ni than the granitic rocks analysed by Sandell and Goldich (1943) and very much less than the Skaergaard granophyres.

Cobalt (Figs. 4*a*, 4*b*)

Nockolds and Allen (1956) have shown that in many of the iron-rich

Table 6(a). Modal analyses of Eigg pitchstones (vol. per cent)

	Glass	Feldspar	Quartz	Pyroxene	Olivine	Iron oxides
1	97·6	1·0	—	0·2	0·2	—*
2	95·6	0·7	3·4	<0·1	0·2	—
3	79·3	19·2	—	1·0	—	0·5

* Includes 1·0 per cent calcite.

Table 6(b). Eigg pitchstones

	r	(1)	(2)	(3)	(3G)
Si^{4+}	0·42	333×10^3	357×10^3	315×10^3	328×10^3
Al^{3+}	0·51	69×10^3	64×10^3	82×10^3	77×10^3
Ti^{4+}	0·68	3×10^3	2×10^3	4×10^3	4×10^3
Fe^{3+}	0·64	5×10^3	7×10^3	10×10^3	9×10^3
Mg^{2+}	0·66	1×10^3	1×10^3	4×10^3	3×10^3
Fe^{2+}	0·74	33×10^3	13×10^3	10×10^3	3×10^3
Na^{+}	0·97	41×10^3	35×10^3	37×10^3	35×10^3
Ca^{2+}	0·99	8×10^3	7×10^3	9×10^3	7×10^3
K^{+}	1·33	25×10^3	21×10^3	52×10^3	50×10^3
P^{5+}	0·35	200	200	500	500
Ga^{3+}	0·62	25	18	15	15
Cr^{3+}	0·63	*	4	*	*
V^{3+}	0·74	10	15	20	15
Nb^{5+}	0·69	15	15	<10	<10
Mo^{4+}	0·70	1·1	1·6	1·2	1·5
Sn^{4+}	0·71	1·1	1·6	2·5	—
Li^{+}	0·68	25	9	25	25
Ni^{2+}	0·69	1·3	1·1	1·2	0·2
Co^{2+}	0·72	1·7	0·3	2·4	0·3
Cu^{2+}	0·72	10	4	2·5	3
Zn^{2+}	0·74	210	87	70	80
Zr^{4+}	0·79	415	390	690	665
Mn^{2+}	0·80	1500	500	800	800
Y^{3+}	0·92	40	20	30	30
Cd^{2+}	0·97	0·34	0·23	0·15	0·14
La^{3+}	1·14	110	150	110	150
Sr^{2+}	1·12	60	390	60	45
Pb^{2+}	1·20	15	26	22	12
Ba^{2+}	1·34	1300	2200	1500	900
Rb^{+}	1·47	110	140	130	160
S		330	180	180	—
As		1·9	0·2	0·8	—
Fe		98	95	83	80
Mg		2	5	17	20
Fe		36	26	18	16
Mg		1	1	3	3
Alk		63	73	79	81
Position		12·7	13·2	14·4	14·9

An asterisk indicates that the element is below the limit of sensitivity which for Cr is (1) and for Li (1) p.p.m. The limit for the chemical determinations of Co is 0·2 p.p.m.
A dash indicates that the sample was not analysed.
Position refers to the value of the factor $[(\frac{1}{3}Si + K) - (Ca + Mg)]$
For the key to the analyses see p. 221.

Table 7. Average concentration of Mo

	(p.p.m.)
7 Arran pitchstones (Table (4)b)	1·6
14 Icelandic pitchstones (Table (5)b)	2·5
18 volcanic glasses (Kuroda and Sandell, 1954, Table 2)	2·5
12 rhyolites and felsites (Kuroda and Sandell, 1954, Table 2)	1·7
61 granites (Kuroda and Sandell, 1954, Table 3)	1·0
Skaergaard acid granophyre sills (Wager and Mitchell, 1951, Table D)	1–3

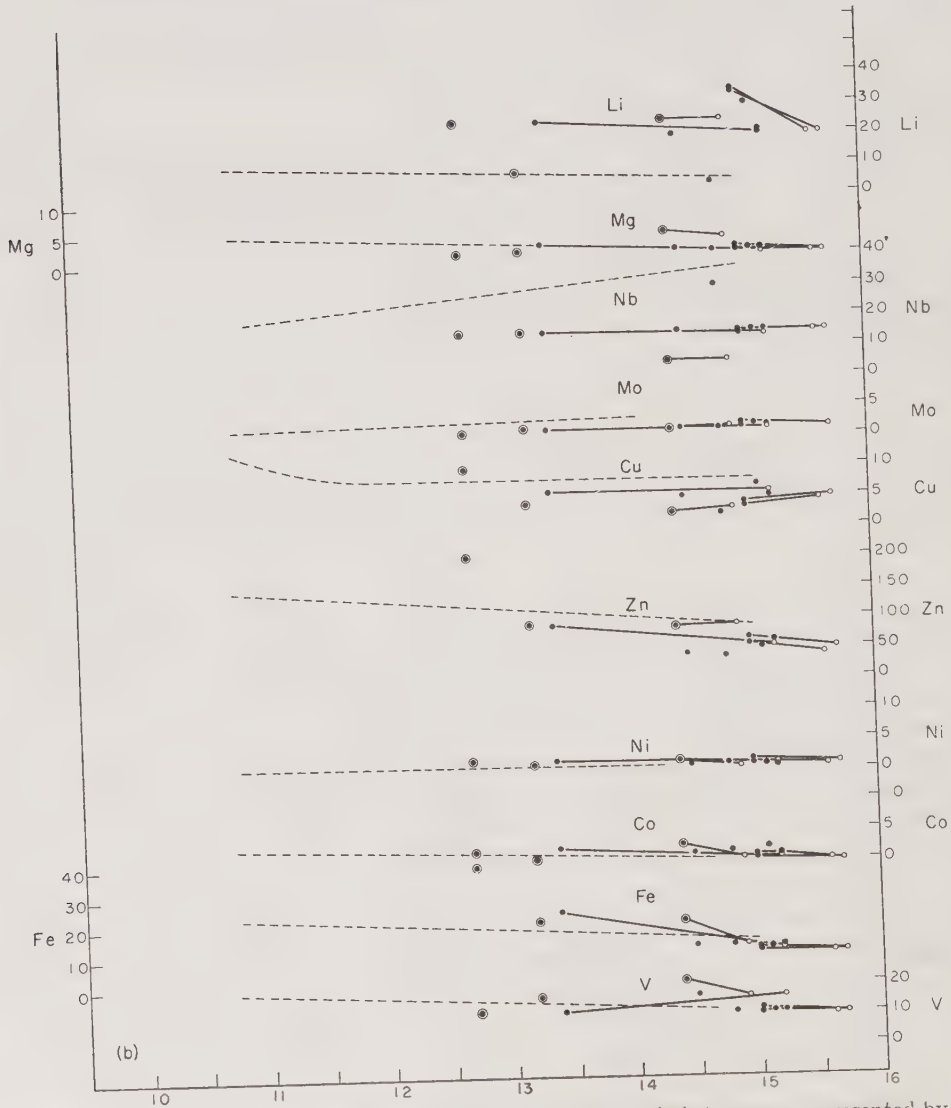


Fig. 4(b). The Arran and Eigg pitchstones. The three Eigg pitchstones are represented by solid circles in open circles. The dashed lines represent the Icelandic trend for each element (Fig. 4a).

tholeiitic series Ni is eliminated more rapidly than Co along the supposed liquid line of descent, so that many intermediate rocks have higher Co than Ni; this relationship may also exist in the acid end members (LUNDEGARDH, 1949), but both elements have normally fallen below the sensitivity of the spectrographic method. The averages of the Arran and Icelandic pitchstones show that Co is more abundant than Ni (Table 8), but the difference is only slight for the Arran group.

In all cases the British and Icelandic residual glasses contain less Co than their pitchstones, the phenocryst minerals being enriched in relation to the liquids. The

Table 8. Average concentration of Ni and Co

	Ni (p.p.m.)	Co (p.p.m.)
7 Arran pitchstones (Table 5(b))	1·1	1·4
14 Icelandic pitchstones (Table 4(b))	0·7	1·3
20 granitic rocks (SANDELL and GOLDICH, 1943)	5·8*	3·0
Skaergaard acid granophyre (WAGER *et al.*, 1957, Table 5)	28·0	6·1
Skaergaard sixth liquid (granophyre)(WAGER and MITCHELL, 1951, Table 10)	8·0	5·0

* Average of nineteen acid rocks.

phenocrysts are also enriched in Co relative to Ni as the residual glasses generally have an excess of Ni over Co. As Ni is in excess of Co in the ilmenomagnetite micro-phenocrysts (Table 3), the iron-rich pyroxene and olivine phenocrysts will of necessity have a considerable excess of Co to Ni in order to preserve the greater relative concentration of Co in the phenocrysts as a whole, and similar enrichment of Co to Ni in the early-formed silicate minerals is found in the Skaergaard fayalite ferrogabbros (WAGER and MITCHELL, 1951, Table B).

Co in both the Icelandic and Arran pitchstones decreases with increase in the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ and the averages of both groups are given in Table 8.

Copper (Figs. 4*a*, 4*b*)

Although Cu in igneous rocks may be related to the content of S (WAGER *et al.*, 1957, p. 877) there is not always a close relation (SANDELL and GOLDICH, 1943, p. 175). The lack of correspondence between the concentrations of Cu and S in these pitchstones has been noted in the discussion on sulphur.

The study of the distribution of Cu in the Skaergaard intrusion (WAGER *et al.*, 1957) shows that in the later stages of fractionation Cu is enriched in the minerals compared to the liquids, and in the late acid granophyre, Cu is equally distributed between the iron sulphide and silicate phases.

The Icelandic and British pitchstones analyses indicate that the phenocrysts are not greatly enriched or impoverished in Cu compared to their liquids. The British residual glasses, however, all show slight enrichment in Cu, whereas the Icelandic liquids behave irregularly with respect to their phenocrysts.

The Icelandic pitchstones as a group show a decrease in Cu as the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, whereas Cu in the British pitchstones remains

approximately constant with increase in the factor. The concentration of Cu in the Icelandic pitchstones and obsidians is greater than in those from Arran, and the averages are tabulated below together with comparative data.

There seems to be a small regional variation between the Icelandic and Arran pitchstones, both groups being low in Cu compared to the Skaergaard acid granophyres and American granites.

Table 9. Average concentration of Cu

	(p.p.m.)
7 Arran pitchstones (Table 5(b))	5
14 Icelandic pitchstones (Table 4(b))	9
20 granites and rhyolites (Sandell and Goldich, 1943)	16
Skaergaard acid granophyre (Wager *et al.*, 1957)	136

Zinc (Figs. 4*a*, 4*b*)

The ionic radius of Zn^{2+} (0·74 Å) is similar to that of Fe^{2+} (0·74 Å), so that Zn is camouflaged in ferrous iron minerals (Table 3), and on the basis of electronegativity, Ringwood (1955a) suggests that Zn becomes concentrated in residual magmas relative to ferrous iron as has been found by Sandell and Goldich (1943, p. 173).

The Icelandic and the Arran residual glasses generally contain less Zn than their respective pitchstones, the 5 per cent or so of phenocrysts being enriched in Zn in relation to the liquids. Both groups of pitchstones show a steady decrease in Zn as the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ increases, although the Arran Zn curve lies below that of the Icelandic pitchstones, and the averages of the two groups presented in Table 10 indicate a distinct regional variation. One of the Eigg pitchstones (Table 6(b), no. 1) is relatively rich in Zn, and in this respect is similar to the Icelandic group.

Table 10. Average concentration of Zn

	(p.p.m.)
7 Arran pitchstones (Table 5(b))	52
14 Icelandic pitchstones (Table 4(b))	125
70 granitic rocks (Wedepohl, 1953, p. 122)	45
23 basaltic rocks (Wedepohl, 1953, p. 116)	121

The Icelandic pitchstones are unusually rich in Zn, the level of Zn being comparable to many basic igneous rocks, so that if, as Sandell and Goldich (1943, pp. 172–173) suggest, there is a correlation between Zn and Fe or Mn in basic rocks, then the Icelandic basalts and andesites will also be correspondingly rich in Zn.

As the determinations of Zn are relatively precise, it is of interest to calculate the level of Zn in the unanalysed iron-rich pyroxene and olivine phenocrysts of the pitchstones which have had their residual glasses analysed. Using an average value for the Zn contents of the feldspar phenocrysts (Table 1), and the ilmenomagnetite microphenocrysts (Table 3), together with the modal analyses and the respective tabulated values of Zn in the pitchstones and their residual glasses (Tables 4(b), 5(b) and 6(b)) the ferromagnesian silicate phenocrysts (olivine and/or pyroxene)

contain on average 1500 p.p.m. Zn. The magnesian pyroxene phenocrysts (Carmichael, 1960a) of the Eigg sub-acid porphyritic pitchstone (Table 6(b), no. 3) contain only about 100 p.p.m. Zn; this value is considered fairly reliable as the coexisting feldspar and ilmenomagnetite phenocrysts have been analysed (Tables 1, 3). Wedepohl (1953, p. 107) presents the analyses of four magnesian pyroxenes which range from 16 to 79 p.p.m. Zn, and are thus of the same order of magnitude

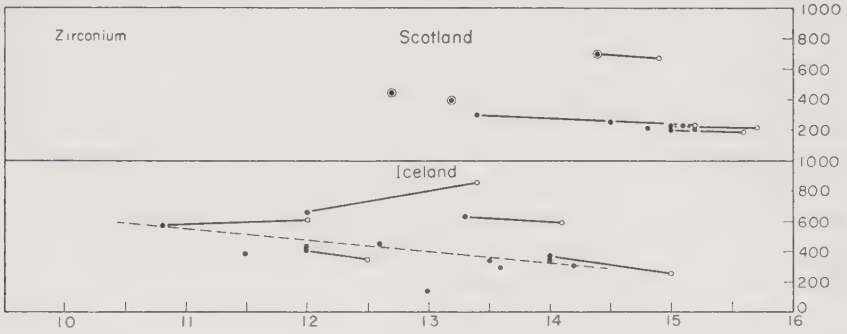


Fig. 5. Variation in zirconium for the Icelandic and British pitchstones (solid circles) and their respective residual glasses (open circles). Solid circles enclosed in open circles represent Eigg pitchstones. Values in p.p.m.

as the Eigg pyroxene phenocrysts. There appears to be no data on Zn in iron-rich olivines and pyroxenes, but the derived value (1500 p.p.m.) does not seem unreasonable.

Zirconium (Fig. 5)

Wager and Mitchell (1951, pp. 192–193) found that Zr was concentrated in the final acid liquids of the Skaergaard intrusion, in which its solubility is believed to be 300–400 p.p.m. The low solubility of Zr in granitic magma has also been discussed by Vogt (1921) and an explanation of the concentration of Zr in residual magmas has been given by Ringwood (1955b).

Minute, very sporadic crystals of zircon may be present in the Icelandic pitchstones, and accordingly were found in the heavy mineral concentrates of the Icelandic pitchstones, whereas the impression was obtained that zircon was almost entirely absent from the heavy mineral concentrates of the Arran pitchstones. In the pitchstones which have not had their heavy minerals separated, the presence or absence of zircon is difficult to establish under the microscope, and the authors believe that it is not always present in the Icelandic pitchstones, and almost never present in the Arran pitchstones (cf. Tyrrell, 1928, pp. 223–233).

With two exceptions the residual glasses all have lower contents of Zr than their respective pitchstones; both exceptions contain basaltic material which presumably contains only a small amount of Zr (the Zr figure for the residual glass no. 3(; (Table 4(b)), however, does seem to be too high). The decrease in Zr in the residual glasses indicates that the phenocrysts are relatively enriched in Zr, and as Wager and Mitchell (1951, Table B) indicate that Zr does not enter the feldspars or the iron-rich pyroxenes and olivines, a few zircons may exist as micro-phenocrysts in all the porphyritic Icelandic and Arran pitchstones.

The average Zr content of thirteen Icelandic pitchstones (400 p.p.m.) is higher than that of seven from Arran (230 p.p.m.) and although the Icelandic samples show far greater variation, it is considered that a real distinction exists.

The residual glasses should give an indication of the solubility of Zr in acid magma as represented by these pitchstones. The Icelandic residual glasses show a rather wide range of Zr concentration (250–600 p.p.m.) (no. 3G, Table 4 being neglected), the average (440 p.p.m.) being twice as high as that of the Arran residual glasses (200 p.p.m.). It is unlikely that the solubility of Zr can vary so much, and unless the Arran liquids are unsaturated, the mean of 300 p.p.m. is taken to indicate the approximate solubility of Zr in acid melts of similar composition to these north Atlantic pitchstones. The solubility of Zr in the Skaergaard acid liquids is believed to be 300–400 p.p.m. as noted above (Wager and Mitchell, 1951). The higher level of Zr in the sub-acid residual glass of the Eigg pitchstone (Table 6(b), no. 3G) indicates the higher solubility of this element in more alkali-rich siliceous magmas. The other two Eigg pitchstones are similar to those from Iceland in respect of their Zr concentration.

Yttrium and lanthanum (Figs. 6*a*, 6*b*)

Wager and Mitchell (1951, Table 10) have found that Y and La become concentrated in the Skaergaard acid granophyres, and Nockolds and Allen (1956) have similarly shown that Y becomes enriched in the acid members of the British tholeiitic series.

The British and Icelandic residual glasses generally have the same concentration of Y as their pitchstones, the phenocrysts being neither enriched or impoverished in Y. There is no variation of Y in either group as the factor

$$[(\tfrac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$$

increases, but the Icelandic Y curve is slightly higher than the Arran curve, and the average (45 p.p.m.) correspondingly higher than that (32 p.p.m.) of Arran.

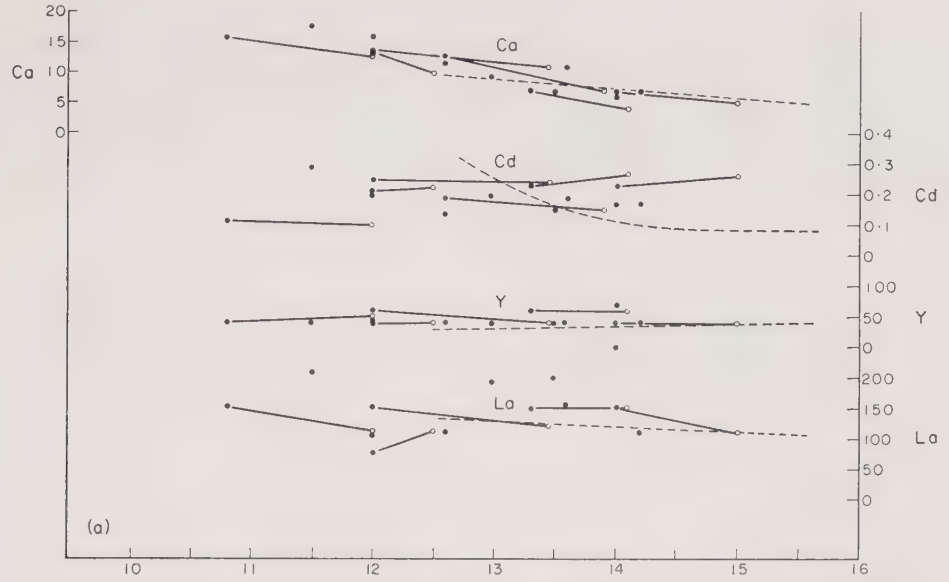
There is a tendency for the Icelandic and the Arran residual glasses to be impoverished in La compared to the phenocrysts, La (and Y) probably being camouflaged by Ca in the iron-rich pyroxenes (cf. Wager and Mitchell, 1951, Table B) rather than in the feldspars. The Eigg (Table 6(b), no. 3G) and one Icelandic (Table 4(b), no. 4) residual glass show the reverse relationship. The group of Icelandic pitchstones show a considerable scatter of La values, and there is little variation in either group of pitchstones with increase in the factor

$$[(\tfrac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$$

The Icelandic La curve is higher than the Arran curve and the average (165 p.p.m.) accordingly higher than the Arran average (120 p.p.m.).

Cadmium (Figs. 6*a*, 6*b*)

Cd is known to be enriched in hydrothermal minerals and residual granitic melts (Rankama and Sahama, 1950), the behaviour of Cd^{2+} (0·97 Å) being in accord with its greater electronegativity compared to Ca^{2+} (0·99 Å) (Ringwood, 1955a); Vincent and Bilefield (1960), however, have illustrated the lack of geochemical



Figs. 6(a) and 6(b). Variation in calcium, cadmium, yttrium and lanthanum. Values for Cd, Y and La in p.p.m. Pitchstones (solid circles) are joined to their respective residual glasses (open circles).

Fig. 6(a). The Icelandic pitchstones. The dashed lines represent the British trend for each element (Fig. 5b).

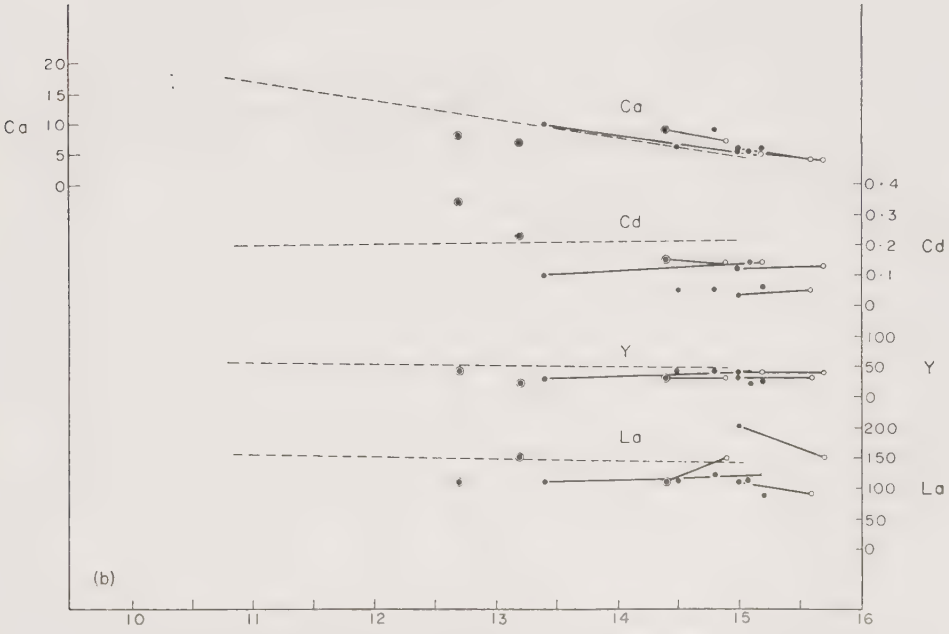


Fig. 6(b). The Arran and Eigg pitchstones. The three Eigg pitchstones are represented by solid circles in open circles. The dashed lines represent the Icelandic trend for each element (Fig. 5a).

coherence between Cd and Ca. Data on the concentration and distribution of Cd in igneous rocks is limited. Sandell and Goldich (1943) provide the results of eight determinations on igneous rocks, and they suggest that Cd may be slightly more abundant in basic than acid rocks; however, the Skaergaard intrusion shows a four-fold increase in Cd in the late granophyric differentiates compared to the initial gabbro parent (Vincent and Bilefield, 1960).

Table 11. Average concentration of Cd

	(p.p.m.)
7 Arran pitchstones (Table 5(b))	0·08
14 Icelandic pitchstones (Table 4(b))	0·20
13 American granites (Sandell and Goldich, 1943)	0·14
2 Skaergaard acid granophyres (Vincent and Bilefield, 1960)	0·50

The Icelandic residual glasses show no consistent trend of enrichment or impoverishment in Cd compared to their pitchstones (phenocrysts) and the Icelandic pitchstones as a group shows little variation in Cd with increase in the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ although over the limited range of composition represented by these pitchstones, great variation is not to be expected.

The Arran pitchstones behave similarly to the Icelandic specimens, the residual glasses showing no consistent relationship to their pitchstones. The general Cd trend of the British pitchstones is upset by the high Cd values of two Eigg pitchstones (Table 6(b), nos. 1 and 2), which in respect of their Cd content are similar to the Icelandic group. The higher level of Cd in the Icelandic pitchstones compared to the Arran pitchstones is clearly shown in Fig. 5 and the averages of both groups are set down in Table 11.

Sandell and Goldich (1943) found that the Zn:Cd ratio remains fairly constant in a suite of basic and acid rocks, the ratio having an average value of 500:1. The pitchstones and residual glasses from Arran, Eigg and Iceland show a rather large spread of values for this ratio, and the average of thirty-four analysed pitchstones and residual glasses from all localities is 650:1.

Calcium and strontium (Figs. 7*a*, 7*b*)

The British and Icelandic residual glasses all contain less Ca than their pitchstones, the phenocrysts therefore being enriched in Ca relative to the liquids. Both groups of pitchstones show a steady decrease in Ca with increase in the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$, but the Icelandic group show the more rapid elimination of Ca.

The phenocrysts of all the British and Icelandic pitchstones are enriched in Sr in relation to their liquids (residual glasses), and both groups of pitchstones decrease in Sr with increase in the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$. The British Sr curve is higher than the Icelandic, due to the anomalously high Sr of one of the Eigg pitchstones (Table 6(b), no. 2), but the Arran average (85 p.p.m.) is less than that (120 p.p.m.) of the Icelandic pitchstones. The Sr $\times$ 100/Ca ratio shows a rather irregular variation in the Arran and Icelandic pitchstones and also in the residual glasses.

Sodium (Figs. 7*a*, 7*b*)

The British and Icelandic residual glasses are erratic with respect to Na, some being slightly enriched and others slightly impoverished in relation to their phenocrysts, but in the whole Icelandic group, Na shows a steady increase as the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, whereas the British pitchstones show a slight decrease in Na. This decline has been found by Nockolds and Allen (1956, Fig. 44e) in the British main trend where Na passes through a weak maximum.

Lead (Figs. 7*a*, 7*b*)

The Icelandic residual glasses are all considerably impoverished in Pb compared to their phenocrysts; the feldspars and ilmenomagnetites (Tables 1 and 3) are both low in Pb, and as Pb was not detected (less than 10 p.p.m.) in the iron-rich pyroxenes and olivines of the Skaergaard fayalite ferrogabbros (Wager and Mitchell, 1951, Table C) Pb is unlikely to be abundant in the pyroxene and olivine phenocrysts of these pitchstones. The total contribution of the phenocrysts of the Icelandic pitchstones is of the order of 500 p.p.m. Pb, so that a mineral containing Pb as a major component may exist in these pitchstones. Goldschmidt (1954) suggests that much of the Pb content of igneous rocks may be caused by PbS, and Sandell and Goldich (1943) conclude that Pd in igneous rocks is not all held in the silicate minerals. It would seem then that the small quantities of sulphide minerals present in many of these pitchstones may hold considerable quantities of Pb.

The Arran and Eigg residual glasses also show a decrease in Pb compared to their respective pitchstones, and it is suggested that lead may similarly be concentrated in the rare sulphide minerals.

In the Icelandic pitchstones as a group Pb remains approximately constant as the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases, but the British pitchstones, which have a rather more variable Pb content, indicate that Pb may slightly decrease as the factor $[(\frac{1}{3}\text{Si} + \text{K}) - (\text{Ca} + \text{Mg})]$ increases.

The Icelandic pitchstones contain less Pb than the Arran representatives, and the averages of the two groups is given in Table 12 together with comparative data.

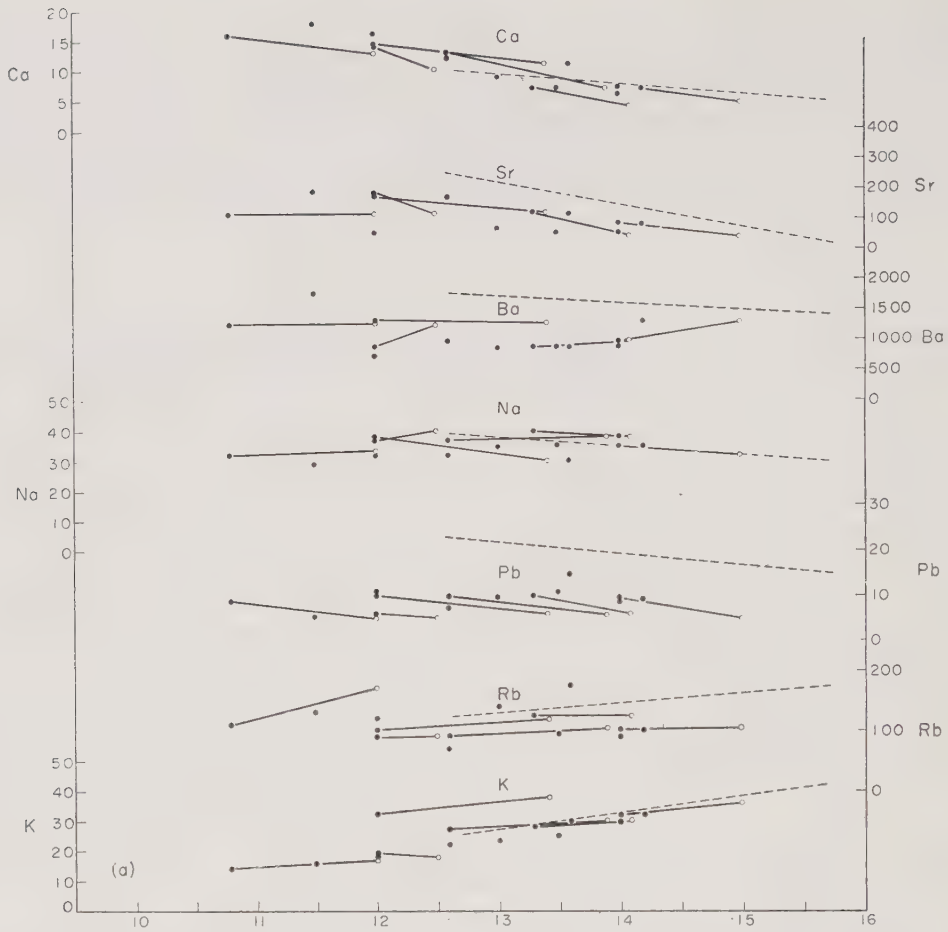
The Icelandic pitchstones have an unusually low content of Pb, similar to that of many basic rocks, and show that considerable regional variation may exist in the north Atlantic Tertiary. It is of interest that in the acid granophyres of the Skaergaard intrusion (Wager and Mitchell, 1951, Table D) Pb was below the limit of detection (10 p.p.m.).

Sandell and Goldich (1943) found that Pb tends to be concentrated in acid rocks, and that K may be used as an index element, the Pb × 1000/K ratio having a constant value (0·5) (Sandell and Goldich, 1943, Fig. 6). The average value of this ratio for the Icelandic and Arran pitchstones respectively is 0·4 and 0·5.

Barium (Figs. 7*a*, 7*b*)

Barium tends to be concentrated in residual acid liquids (Wager and Mitchell, 1951, Table 10) and may show preferential enrichment to K in the early formed crystals (Ringwood, 1955a, p. 201).

All the British residual glasses show that Ba is enriched in the phenocrysts (principally feldspar) and the ratio Ba × 100/K is lower in the residual glasses



Figs. 7(a) and 7(b). Variation in calcium, strontium, barium, sodium, lead, rubidium and potassium. Values for Sr, Ba, Pb, and Rb in p.p.m. Pitchstones (solid circles) are joined to their respective residual glasses (open circles).
Fig. 7(a). The Icelandic pitchstones. The dashed lines represent the British trend for each element (Fig. 7b).

Table 12. Average concentration of Pb

	(p.p.m.)
7 Arran pitchstones (Table 5(b))	18
14 Icelandic pitchstones (Table 4(b))	9
29 granites and rhyolites (Sandell and Goldich, 1943)	19
22 basic igneous rocks (Sandell and Goldich, 1943)	9

showing the phenocryst's preferential enrichment in Ba relative to K. Two of the Arran residual glasses (Table 5, nos. 4 and 5) indicate that the phenocrysts may have between 1 and 2 per cent Ba, an improbably high concentration, whereas the computed concentration of Ba in the Eigg feldspar phenocrysts (Table 1, no. 3) is 4000 p.p.m., the determined figure being $>$ 2000 p.p.m. Although the Ba concentration in the phenocrysts of the two Arran pitchstones is unusually high, the British

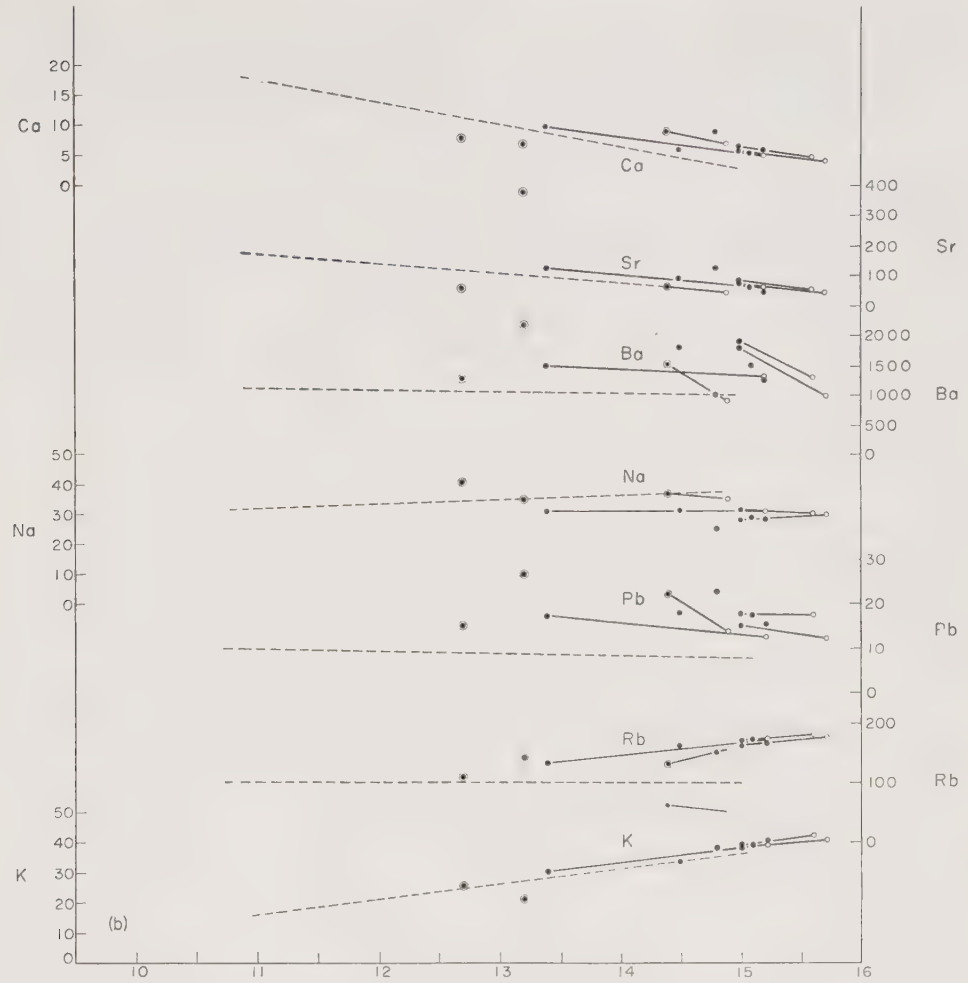


Fig. 7(b). The Arran and Eigg pitchstones. The three Eigg pitchstones are represented by solid circles in open circles. The dashed lines represent the Icelandic trend for each element (Fig. 7a).

trend is in distinct contrast to that of Iceland, where the residual glasses are generally enriched in Ba in relation to their phenocrysts, the enrichment relative to K (Ba $\times$ 100/K) in the phenocrysts being irregular. The contradictory behaviour of Ba is not understood, for the enrichment of Ba in the phenocrysts indicates a maximum in the Ba variation curve, whereas the Icelandic evidence suggests a steady enrichment of Ba in the residual liquids.

Neither group of pitchstones shows much variation in Ba as the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ increases, but the Arran curve is above the Icelandic, and the average (1500 p.p.m.) correspondingly higher than the Icelandic (1100 p.p.m.) average.

Potassium and rubidium (Figs. 7*a*, 7*b*)

K is enriched in both the Icelandic and British residual glasses relative to the

phenocrysts, the Eigg feldspar phenocrysts, however, are enriched in K compared to the liquid (Table 2, no. 3) as is one Icelandic specimen (Table 4(b), no. 4).

Both groups of pitchstones show a steady increase in K as the factor

$$[(\tfrac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$$

increases.

The Icelandic and Arran liquids (residual glasses) show weak or definite enrichment in Rb, but there is little variation of Rb in the Icelandic pitchstones as the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ increases, whereas the British representatives show a steady increase. The Rb $\times$ 1000/K ratio of the Arran pitchstones is remarkably constant and shows no preferential enrichment of K in the phenocrysts, the same lack of enrichment also being found in Iceland, where the values of this ratio show a considerable range, possibly as a result of the abstraction of K by the subsequent hydrothermal alteration (p. 195).

Sulphur (Fig. 8)

Sulphur has only been determined on the pitchstones and obsidians, there being insufficient separated residual glass and phenocryst minerals for analysis.

Vogt's experimental data illustrating the low solubility of S in siliceous liquids has been summarized by Wilson (1953) and more recently Wager *et al.* (1957) have studied the distribution of S in the Skaergaard intrusion, and have used their results to deduce the concentration of S in the successive residual liquids. The analyses of the more acid Skaergaard rocks do not provide data for comparison, as there has been considerable redistribution of the immiscible sulphide liquid phase. The concentration of S in the Skaergaard acid granophyres (ca. 0·1 per cent) (Wager *et al.*, 1957, Table 5) is very much greater than the suspected solubility of S in acid liquids, and Wager *et al.* suggest that the iron sulphide liquid accompanied the expulsion of the final silicate fraction to give rise to the acid granophyres. The deduced concentration of S in the fifth Skaergaard liquid (Wager *et al.*, 1957, Table 9) is 260 p.p.m. which corresponds reasonably well with the average level of 180 p.p.m. S of those acid glasses which being more siliceous may be expected to have a lower solubility of S. It is unknown whether these natural acid glasses are saturated with S, but the small and very sporadic specks of pyrite in many of the Icelandic and British pitchstones suggest that this may be the case.

The concentration of S in both the Icelandic and British pitchstones has been plotted against the factor $[(\frac{1}{3}\mathrm{Si} + \mathrm{K}) - (\mathrm{Ca} + \mathrm{Mg})]$ and shows no clear indication of a decrease in S as the factor increases. There seems to be no convincing difference between the British and Icelandic pitchstones with regard to S; any difference is unlikely if the glasses are in fact saturated with S.

There is no correlation between the concentration of Cu in those pitchstones and that of S. Microscopically pyrite is the only sulphide mineral of importance (Cu being principally concentrated in the ilmeno-magnetite microphenocrysts); this is in agreement with the evidence of the Skaergaard intrusion, where an iron-sulphide liquid develops late in the fractionation history, although the silicate liquid still contains notable amounts of Cu. (Wager *et al.*, 1957).

Arsenic

As has only been determined in the pitchstones and obsidians, there being insufficient separated residual glass and phenocryst minerals for analysis.

The geochemistry of As has been discussed by Onishi and Sandell (1955) who provide the only source of comparable data. They noted that there was no relationship between the concentration of As and any major element, although in some of the Keweenawan lavas, there does seem to be a small corresponding increase of As

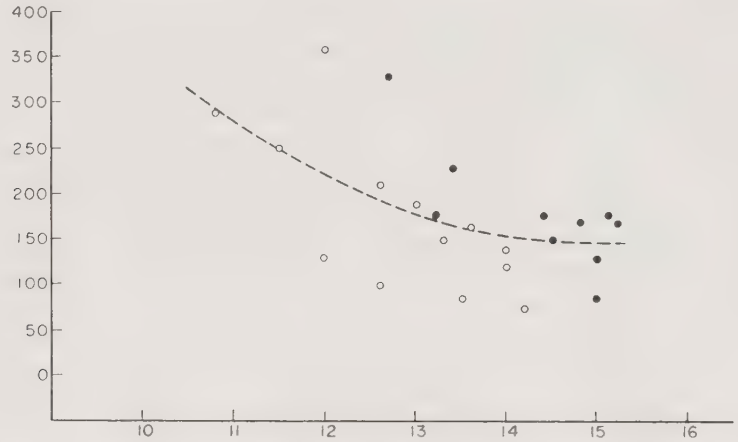


Fig. 8. Variation in S for the British (solid circles) and Icelandic (open circles) pitchstones. Values in p.p.m.

Table 13. Average concentration of As

	(p.p.m.)
7 Arran pitchstones (Table 5(b))	1·8
14 Icelandic pitchstones (Table 4(b))	1·5
12 volcanic glasses (Onishi and Sandell, 1955)	5·9
16 felsites and rhyolites (Onishi and Sandell, 1955)	3·5
50 granites (Onishi and Sandell, 1955)	1·7

with Si. Onishi and Sandell also concluded that there was a complete lack of correspondence between As and S.

The results of the determinations of As for the Arran, Eigg and Icelandic pitchstones (Tables 4(b), 5(b), 6(b)) also show that As does not vary with Si, although these pitchstones represent only a limited range of composition. There is also no correspondence between As and S in these acid glasses.

The results of Onishi and Sandell (1955, p. 11) suggest that there is a considerable decline in the level of As with the rate of cooling of acid rocks. The average values of As obtained by them for volcanic glasses, rhyolites and felsites, and granites is given in the accompanying table together with the corresponding data of these pitchstones.

The low level of As in the north Atlantic pitchstones, and its equivalence to the concentration in the granites of Onishi and Sandell suggests that either As has been lost from the pitchstones before the congelation of the liquid or a regional

variation in the concentration of As exists, so that the granites of the British Tertiary may have lower and hence very small amounts of As.

The ionic radius of As has not been given in the tables for although Onishi and Sandell (1955) believe that As^{3+} (0·58 Å) is predominant, especially in magmas with a low Fe_2O_3:FeO ratio, As^{5+} (0·46 Å) may also exist in natural melts.

Conclusions

The distribution of elements between phenocrysts and the liquids with which they are in equilibrium illustrates the chemical variations to be expected in liquids derived from a parent (higher up the liquid line of descent) by the separation (fractionation) of early-formed crystals. Wager and Deer (1939) and Wager and Mitchell (1951) have calculated the composition of successive liquids which have developed under conditions of strong fractionation during the crystallization of the Skaergaard gabbroic intrusion. The Skaergaard liquids are generally more basic or lie higher up a fractionation sequence than those described here, where the hypothetical results of fractionation caused by the separation of the phenocrysts from their acid liquids provide only a small resultant change in composition. However, it is the direction, rather than the extent of the change that is important, particularly here with regard to the trace elements, and in a small way, the relationship of phenocrysts to liquid and the attendant possible variation under conditions of fractionation, continues the Skaergaard fractionation account into dominantly acid liquids.

In the Icelandic acid liquids (residual glasses)which represent a greater overall range of composition than the Arran liquids, the only major elements to be enriched in relation to the phenocrysts are Si and K. The liquids also show enrichment in the trace elements Rb and Nb, and are weakly enriched in Cd and Ba, although the degree of enrichment is almost within (if not completely for Cd) the variation to be expected through analytical error. All the other determined elements may show very little or considerable enrichment in the phenocrysts.

There is an unusual reduction of Li, Pb, Zr and possibly La in the Icelandic liquids, and as these elements are normally most abundant in late acid liquids (Wager and Mitchell, 1951, Table 10), the concentration of these elements in the phenocrysts indicates that under conditions of thorough crystal fractionation, the variation curves of these elements in successive liquids will show a maximum. The Arran phenocrysts are enriched in Ba unlike those of Iceland, so that under certain conditions (unknown) Ba may also show a maximum. With this exception the Arran acid liquids show the same general relationship to their phenocrysts as those of Iceland.

The relatively large reduction of Pb in the Icelandic and to a lesser extent the Arran liquids compared to the phenocrysts is unusual, and the average calculated concentration of Pb in the Icelandic phenocrysts is approximately 500 p.p.m. As Pb is not believed to enter either the silicate (Table 1), (Wager and Mitchell, 1951, Table B) or the ilmenomagnetite phenocrysts (Table 3) to any great extent, it was concluded that the rare sulphide minerals may contain notable amounts of lead.

The solubilities of Zr and S in acid liquids of similar composition to these pitchstones are deduced to be, respectively, 300 p.p.m. and 180 p.p.m. Both concentrations are in fair agreement with the results of others; WAGER and MITCHELL (1951 p. 192) report 300–400 p.p.m. Zr in the Skaergaard late granophyric

Table 14. Average analyses of Arran and Icelandic pitchstones

	A	B	C
SiO_2	76·5	74·4	75·03
TiO_2	0·23	0·29	0·31
Al_2O_3	12·0	12·8	13·17
Fe_2O_3	0·5	1·1	1·56
FeO	1·2	1·7	0·58
MgO	0·15	0·25	0·15
CaO	0·95	1·6	0·69
Na_2O	3·9	4·7	4·24
K_2O	4·4	3·0	3·85
P^{5+}	100	190	80
Ga^{3+}	13	19	30
Cr^{3+}	3	4	14
V^{3+}	10	15	18
Nb^{5+}	17	26	—
Mo^{4+}	1·6	2·5	1
Sn^{4+}	1·2	2·6	—
Li^{+}	24	11	13
Ni^{2+}	1·1	0·7	8
Co^{2+}	1·4	1·3	5
Cu^{2+}	5	9	20
Zn^{2+}	52	125	—
Zr^{4+}	230	400	850
Mn^{2+}	300	700	ca.150
Y^{3+}	32	45	250
Cd^{2+}	0·08	0·20	0·50
La^{3+}	120	165	240
Sr^{2+}	85	120	350
Pb^{2+}	18	9	<10
Ba^{2+}	1500	1100	1400
Rb^{+}	160	120	160
As	1·8	1·5	—

A. Average of seven Arran pitchstones, Table 5(b).
B. Average of fourteen Icelandic pitchstones, Table 4(b).
C. Skaergaard acid granophyre, WAGER and MITCHELL (1951), Table F. The value for Cd is taken from VINCENT and BILEFIELD (1960).

liquids, and RICKE (1960) obtained an average of 190 p.p.m. S for twenty-four acid glasses.

LUNDEGARDH (1949) has suggested that as the initial crystal fractions of basic magma are enriched in Cr relative to Ni, which in turn is enriched relative to Co, then intermediate and acid rocks derived from a basic parent by crystal fractionation should have these three elements in the following order of abundance, Co > Ni

>Cr. The late acid granophyres of the Skaergaard intrusion (Table 14) do not show this order, but the Skaergaard liquids are perhaps unusual as Cr, Ni and V, which are almost completely removed from the intermediate liquids, become concentrated again in the late acid liquids. Ringwood (1955b) has commented on this unusual behaviour, and suggested that it may be due to the influence of an increasing concentration of volatiles. It is possible that the excess of Ni over Co in some of the residual glasses (liquids) in contrast to the reverse relationship in the liquids plus phenocrysts (pitchstones) is the less complete result of a similar influence.

The averages of the Arran and the Icelandic pitchstone analyses (Table 14) show that Cr>Co>Ni, the concentration of all three elements being lower than in the average of the Skaergaard acid granophyres (Table 14). The values for Cr are perhaps uncertain, as this element falls below the limit of detection in many pitchstones, but it also shows a remarkably high concentration in one Icelandic obsidian (30 p.p.m.) (Table 4(b), no. 7).

The averages of the two groups of pitchstones show a distinct chemical divergence, particularly in the trace elements Nb, Mo, Sn, Cu, Zn, Zr, Mn, Cd, Pb and possibly Ga and Rb. The two Eigg pitchstones (Table 6(b), nos. 1 and 2) are believed to be intermediate in composition, showing affinity both to the Icelandic and Arran groups, and some of the possible geological consequences have been considered elsewhere (Carmichael, 1961).

The cause of the clear chemical distinction between the Icelandic and Arran pitchstones (Table 14) must be closely connected with the origin and history of the acid liquids. The origin of the north Atlantic Tertiary pitchstones cannot be considered here, and whether or not they are the derivatives of a basaltic parent is unknown. The chemical evidence presented here unfortunately does little to indicate their origin, but the presence of xenocrysts in some of the Arran porphyritic pitchstones (Carmichael, 1961) indicates at least a certain degree of contamination.

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Key to Analyses

Icelandic pitchstones and obsidians (Table 4(b)).

(1) Pitchstone margin of acid lava, Thingmuli, E. Iceland. G. 87 [anal. 3R, Table 6, (1960a)*].
(1G) Residual glass from G.87 [anal. 3G, Table 6, (1960a)].
(2) Glassy top of acid lava, Thingmuli, E. Iceland. H.98 [anal. G, Table 3, (1961)†].
(3) Pitchstone margin of intrusion, Skruthur, E. Iceland. P.258 [anal. 7R, Table 6, (1960a)].
(3G) Residual glass from P.258 [anal. 7G, Table 6, (1960a)].
(4) Pitchstone margin of dacite lava, Rauthaskritha, E. Iceland. 1C.3 [anal. 9R, Table 6, (1960a)].
(4G) Residual glass from 1C.3 [anal. 9G, Table 6, (1960a)].

*(1960a) and †(1961) refer to Carmichael (1960a) and (1961).

(5) Glassy top of acid lava, Berufjordur, E. Iceland. P.408 [anal. H, Table 3, (1961)].
(6) Pitchstone margin of acid dyke, Thingmuli, E. Iceland. G.151 [anal. 6R, Table 6, (1960a)].
(6G) Residual glass from G.151 [anal. 6G, Table 6, (1960a)].
(7) Obsidian, post-glacial, Hrafntinnurhyggur, Iceland. 1C.2 [anal. J, Table 3, (1961)].
(8) Pitchstone (vesicular) cone-sheet, Thingmuli, E. Iceland. H.49 [anal. K, Table 3, (1961)].
(9) Pitchstone margin of Sellatur plug, E. Iceland. E.868. [anal. 4R, Table 6, (1960a)].
(9G) Residual glass from E.868 [anal. 4G, Table 6, (1960a)].
(10) Glassy top of acid lava, Seydisfjordur, E. Iceland. E.663 [anal. L, Table 3 (1961)].
(11) Glassy top of acid lava, Faskrudsfjordur, E. Iceland. P.127 [anal. M, Table 3, (1961)].
(12) Pitchstone margin of intrusion, Bondolfur, E. Iceland. P.186 [anal. 8R, Table 6, (1960a)].
(12G) Residual glass from P.186 [anal. 8G, Table 6, (1960a)].
(13) Obsidian pebbles, top of acid lava, Bondolfur, E. Iceland. P.192 [anal. N, Table 3, (1961)].
(14) Pitchstone dyke, Thingmuli, E. Iceland. G.239 [anal. O, Table 3, (1961)].

Arran pitchstones (Table 5(b)).

(1) Pitchstone, Glen Shurig, Arran. AC.7 [anal. 10R, Table 6, (1960a)].
(1G) Residual glass from AC.7 [anal. 10G, Table 6, (1960a)].
(2) Pitchstone, Judd's no. 2 dyke, Tormore, Arran. AC.20 [anal. A, Table 1, (1961)].
(3) Pitchstone sill, north of Drumadoon Pt., Arran. AC.8 [anal. B, Table 1, (1961)].
(4) Pitchstone, Judd's no. 1 dyke, Tormore, Arran. AC.12 [anal. 2R, Table 6, (1960a)].
(4G) Residual glass from AC.12 [anal. 2G, Table 6, (1960a)].
(5) Pitchstone, Brodick School, Arran. AC.6. [anal. 5R, Table 6, (1960a)].
(5G) Residual glass from AC.6 [anal. 5G, Table 6, (1960a)].
(6) Pitchstone, lower scarp, Dun Fionn, Arran. AC.19 [anal. C, Table 1, (1961)].
(7) Sill, Cluachland shore, Arran. AC.5 [anal. D, Table 1, (1961)].

Eigg pitchstones (Table 6(b)).

(1) Pitchstone dyke, Rudh' a Chromain, Eigg. EC.13 [anal. E1, Table 1, (1961)].
(2) Pitchstone margin of Cleadale felsite, Eigg. EC.10 [anal. E2, Table 1, (1961)].
(3) Pitchstone, Sgurr of Eigg. EC.20 [anal. 1R, Table 6, (1960a)].
(3G) Residual glass from EC.20 [anal. 1G, Table 6, (1960a)].

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Abundance and distribution of alkali elements in Victorian australites

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Abstract—New determinations of Li, Na, K, Rb and Cs for eight australites from Victoria average 41 p.p.m. Li, 0·81% Na, 1·76% K, 73 p.p.m. Rb and 2·1 p.p.m. Cs. These figures are lower than the averages for tektites from localities west of Victoria, and extend the previously described decrease in concentration of the alkali elements from west to east across Australia (Taylor, 1960). The overall average composition for 24 australites analysed here and previously (Taylor, 1960) is 42 p.p.m. Li, 0·90% Na, 1·85% K, 81 p.p.m. Rb and 2·5 p.p.m. Cs(K/Rb = 231). A close coherence exists between all pairs of the alkali elements, similar to the classical K/Rb relationship, and is interpreted as due to a physical mixing of two parent components. The average concentrations of the alkali elements are consistent with derivation from a mixture of 75% shale (less water and CO_2) and 25% SiO_2, with possibly some small selective loss of K, Rb and Cs during initial melting.

Introduction

Determinations of the alkali elements, Li, Na, K, Rb and Cs in 14 australites from Western, Central and South Australia have been published previously (Taylor, 1960). It was observed that there was a regional variation in composition, a decrease in concentration of these elements being shown toward the east. In order to see whether this tendency persisted, or was reversed, eight tektites from Victorian localities have been analysed. No specimens from Tasmania or New South Wales were available. It was also desired to know if the highly significant positive correlation between all the alkali elements was shown by the present samples, and, in addition, to obtain further data for computing average values for australites.

Analytical Methods

The sample preparation was carried out in the manner described in the previous paper, except that all samples were first cleaned by boiling in 5 N. HCl to remove adhering claylike material. The samples analysed previously had been cleaned before receipt. The analytical procedures for sodium and potassium were identical with those described (Taylor, 1960). Attention is drawn to an error in the value given in Table 1 of that paper for the sodium content of U.S.B.S. 98, which should read 7·96 per cent. The determination of lithium, rubidium and caesium was similar to the methods used previously, except that Kodak IL plates were used in place of IN, and Li 8126 was read in place of Li 6103.

Samples analysed previously were included to ensure that the two sets of results would be comparable.

Discussion

The sample localities, description of specimens, refractive indices and specific gravities are given in Table 1. Analytical determinations are given in Table 2. An extra sample from Kalgoorlie, Western Australia is included, as well as data for cores of two flanged button forms (Nos. 1(B) and 625(A)) published previously (Taylor, 1961). The data for three flanges given in the same paper are not included here, for they contain significantly lower amounts of the alkali elements than do the

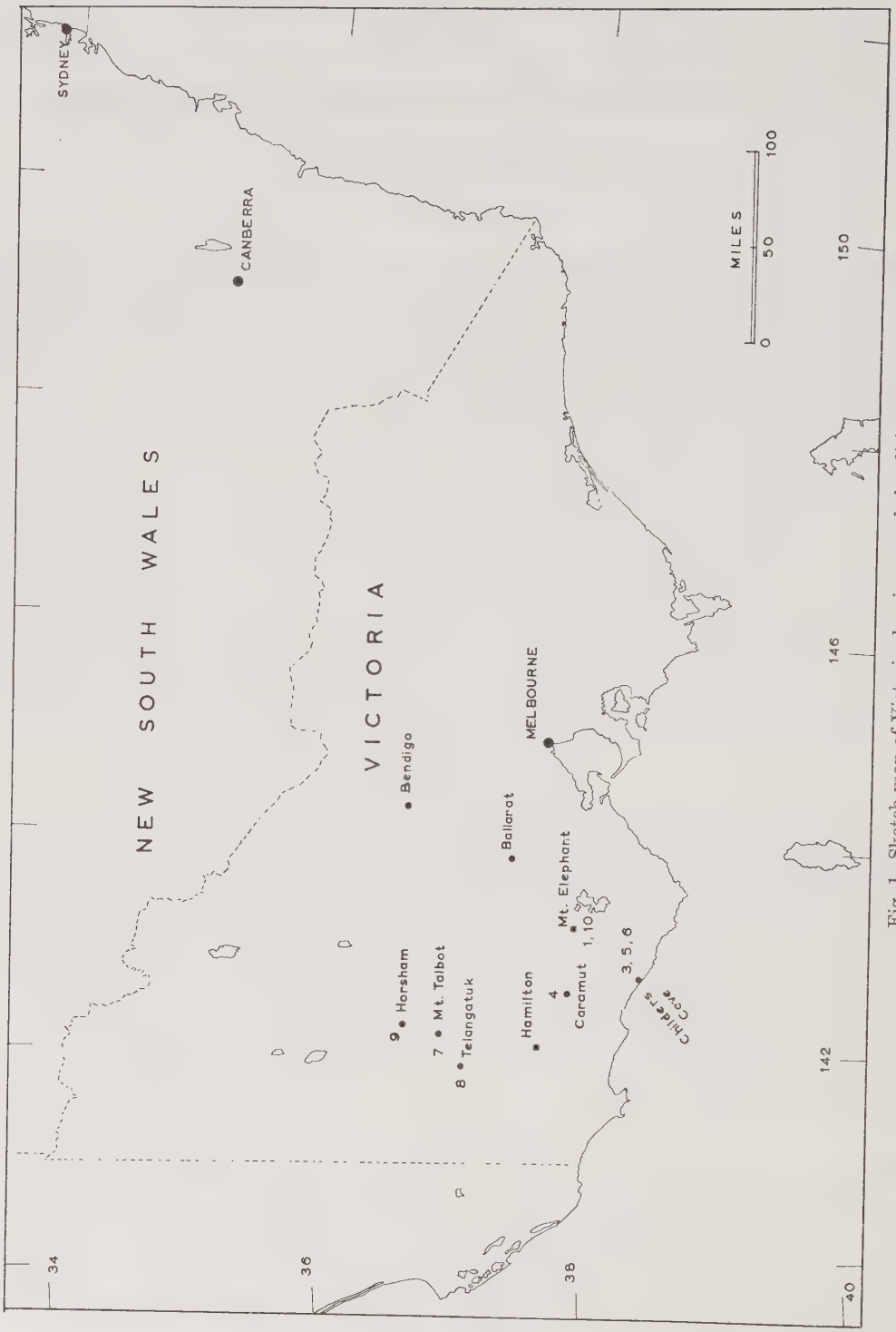

Fig. 1. Sketch map of Victoria showing sample localities.

cores.* For this reason they are not used to compute averages, nor calculate the correlation coefficients. The average of the present determinations, and the analytical precision is also given in Table 2, followed by the average of the previous 14 determinations, the average of all 24 determinations, the spread of these, expressed as a relative deviation, and the overall analytical precision, also given as *C*.

Table 1.

Sample number	Locality	Type	Weight gms.	Refractive index	Specific gravity
1(B)	Mount Elephant, Victoria.	Button core	6·21	1·503	2·399
3	Childers Cove, Victoria.	Lens.	2·12	1·502	2·375
4	Caramut, Victoria.	Round core	13·28	1·511	2·426
5	Childers Cove, Victoria.	Lens fragment.	0·71	1·501	2·292
6	Childers Cove, Victoria.	Fragment.	1·22	1·498	2·348
7	Mt. Talbot, Victoria.	Lens.	1·76	1·502	2·352
8	Telangatuk, Victoria.	Boat	16·85	1·500	2·401
9	Horsham, Victoria.	Dumb bell (broken)	3·27	1·503	2·394
391	Kalgoorlie district, Western Australia.	Round core.	4·63	1·512	2·405
625(A)	Charlotte Waters, Central Australia.	Button core	5·43	1·508	2·408

Table 2. Analytical results

Sample number	Lithium (p.p.m.)	Sodium (%)	Potassium (%)	Rubidium (p.p.m.)	Caesium (p.p.m.)	K/Rb
1	37	0·81	1·73	73	1·6	237
3	37	0·73	1·65	67	1·1	246
4	45	0·86	1·88	75	2·7	251
5	43	0·80	1·66	62	2·4	268
6	40	0·76	1·69	73	2·4	232
7	40	0·82	1·79	75	2·3	239
8	42	0·89	1·86	75	2·0	248
9	41	0·82	1·78	80	2·2	223
391	44	1·05	1·99	90	3·1	221
625	47	0·89	1·86	90	2·9	207
Average	42	0·84	1·79	76	2·3	237
Analytical precision (*C*)	5·4%	0·5%	0·4%	5·8%	18·0%	
Average of 14 previous determinations	42	0·95	1·89	84	2·7	227
Average of all determinations (24)	*42*	*0·90*	*1·85*	*81*	*2·5*	*231*
Spread of all results (24) (*C*)	9·2%	13·2%	7·5%	12·7%	33·2%	
Overall analytical precision (*C*)	5·8%	2·5%	2·5%	7·6%	14·8%	

The conclusions reported previously (Taylor, 1960) are not altered. The overall average is lower due to the inclusion of the Victorian samples. The spread of the results is greater than the precision of the individual determinations, indicating significant differences in composition between different australites.

* This loss has been interpreted as due to distillation during the second period of melting (Taylor, 1961).

Regional Difference in Composition

Table 3 lists the averages of australites by localities. It can be seen that a general variation in composition exists, with lower concentrations toward the east, although differences exist within each area. This variation of composition with locality is considered as part of an overall trend from west to east. This view regards the australites as due to a single event, whether terrestrial or extra-terrestrial. The alternative opinion that we are dealing with several separate occurrences cannot, of course, be easily disproved without a wealth of statistical data, but has been thought unlikely by most investigators of australites.

Table 3. Average values for australites from Victoria, South and Central, and Western Australia

	Lithium (p.p.m.)	Sodium (%)	Potassium (%)	Rubidium (p.p.m.)	Caesium (p.p.m.)
WESTERN AUSTRALIA (8 tektites)	46	1·04	1·99	90	3·3
SOUTH AND CENTRAL AUSTRALIA (8 tektites)	40	0·87	1·80	80	2·3
VICTORIA (8 tektites)	41	0·81	1·76	73	2·1

Table 4. Coefficients of correlation (r) for the various pairs of elements for 24 australites

	r	Per cent level of significance
Na—K	+0·954	<0·01
K—Rb	+0·901	<0·01
Na—Rb	+0·894	<0·01
Na—Cs	+0·891	<0·01
Rb—Cs	+0·867	<0·01
K—Cs	+0·867	<0·01
Li—Cs	+0·814	<0·01
Na—Li	+0·751	<0·01
K—Li	+0·729	0·01
Rb—Li	+0·679	0·03

Close Association of the Alkali Elements

Table 4 gives the correlation coefficients for the various pairs of elements. All data, from the 24 samples, are included. A highly significant positive correlation exists for all pairs, the level of significance being better than the 0·03 per cent level in all cases. Fig. 2 shows the Na—K relationship. Although the coherence between K and Rb in geological materials and meteorites is well known, there exist no theoretical reasons for a close geochemical coherence of all the alkali elements, which differ widely in ionic size. The explanation for this striking association must be sought in physical, rather than chemical terms. It indicates that the tektites are a mixture of two components in varying amounts. One contains the alkali elements

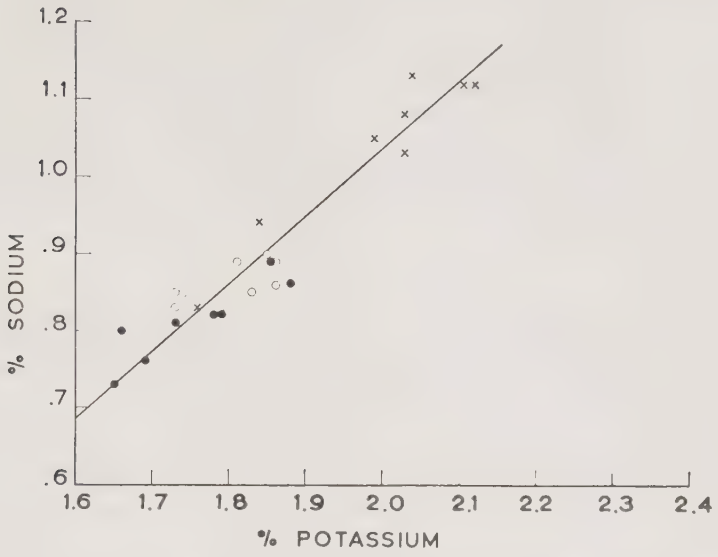

Fig. 2. The close association between sodium and potassium in 24 australites. × Western Australia. ○ South Central Australia. • Victoria.

Table 5. Comparison of the average composition of australites with a mixture of one part SiO_2 and three parts of the "non-volatile" constituents of shales.

	1	2
SiO_2	73·24	73·33
TiO_2	0·54	0·67
Al_2O_3	12·79	11·99
$FeO^{(a)}$	5·04	4·61
MgO	2·03	2·01
CaO	2·58	3·33
Na_2O	1·08	1·21
K_2O	2·69	2·23
Σ	99·99%	99·38%
Li p.p.m.	46	42
Rb p.p.m.	116(100)[b]	81
Cs p.p.m.	4·1	2·5

1. Mixture of three parts of the "non-volatile" constituents of average shale with one part of quartz. See CHERRY and TAYLOR, 1961, Table 1 for sources of data and details of calculations.

The data for the trace elements has been treated in the same manner (multiplied by 100/90·31 to allow for loss of water, etc., followed by dilution with 25% SiO_2). Data for Li from SHAW, (1954), Rb and Cs from HORSTMAN, (1956).

2. Average composition of 9 australites from BARNES (1940), two from BAKER (1956) and 14 australites analysed by H. B. WIIK. The data for the alkali elements (including Na_2O and K_2O) are from the 24 results reported in this paper.

(a) Total Fe expressed as FeO

(b) Rb figure calculated from a K/Rb ratio of 220.

which thus vary sympathetically in concentration as the components vary in amount. Taylor, Sachs and Cherry (1961) and Cherry and Taylor (1961) have described an inverse relation between SiO_2 and the other constituents of tektites, including the alkali elements. This has been interpreted as due to a mixture of quartz, and the less volatile constituents of shale which matches the composition of tektites and from which it is believed they are derived. All the alkali elements would be derived from the shale, and will thus vary together sympathetically, and inversely with the silica content.

A Terrestrial Composition

Cherry and Taylor (1961) have shown that a close match exists between the average composition of tektites and that of a mixture of one part quartz with three parts of average shale (less water, CO_2, SO_3, and organic matter, which total 9·69 per cent). In Table 5 the average composition of australites is compared to that of the mixture, and it can be seen how close the match is for the major elements, including such geologically contradictory features as a combination of 73% SiO_2 and 2% MgO. It is of interest to see if the trace element data support this as well. The geochemical data for Li, Rb and Cs are those used previously (Taylor, 1960). By performing the same calculations as used for the major elements, we get the compositions given in Column 1. The agreement for Li is excellent. Potassium, rubidium and caesium are lower in the australites. If the differences (17 and 39 per cent respectively) are significant, they may be due to some selective distillation of these elements during the initial melting of australites.

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Soil acidity and microelement status

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Introduction

The abundance of microelements in a soil usually depends on the nature of the parent material. The acidity of the circulating water, however, is known to play an important role in the geochemistry of most of the microelements (Goldschmidt, 1954). During the course of an investigation on the total microelement contents of eleven typical Indian soils, it was observed that most of the microelements concentrated in soil of pH values round about 4·5 and about 8·0. To see if the distribution of the microelements observed has any relation to the condition of their precipitation in solutions maintained at different pH values, a preliminary experiment was conducted and the results obtained are discussed in relation to the sorption properties of hydroxides that are likely to form.

Experimental

Eleven soil samples representing the three major soil groups of India, namely, alluvial soil (pH 7·6 to 8·4), black soil (pH 7·9 to 8·6) and laterite soil (pH 4·1 to 5·8), were studied. Boron and manganese were determined spectrographically (Mehta and Dakshinamurti, 1955); copper and zinc were estimated by Holmes' (1945) method; cobalt was determined by nitroso-R-salt method (Sandell, 1944) and molybdenum by the stannous chloride thiocyanate method (Sandell, 1944); pH was determined in 1 : 2·5 soil–water suspension using a Beckman pH meter with glass electrodes. Three solutions were prepared: the first containing the microelements, manganese ($MnCl_2$, 1000), boron (CH_3BO_3, 300), copper ($CuSO_4H_2O$, 60), cobalt ($CoCl_26H_2O$, 3), zinc [$(CH_3COO)_2Zn\ 2H_2O$, 30] and molybdenum (MoO_3, 5) at concentrations usually present in soils and given in parts per million in parenthesis; the second containing iron ($FeCl_36H_2O$) alone at a concentration of 2000 p.p.m. and the third containing all the microelements along with iron at the concentrations present in the first and second solutions. Calcium at 1000 p.p.m. was added to the microelement solution. Fifty millilitres of each of the solutions were taken and requisite quantities of dilute acetic acid solution or sodium hydroxide solution were added as to maintain them at different values of pH ranging between 2·0 and 12·0. The precipitates, if any, obtained by keeping the solutions over-night, were filtered, washed, dried at 105°C for 24 hr and weighed.

Results and Discussion

Microelement contents calculated on air dried soil basis are recorded in Fig. 1. The distribution of the microelements shows an accumulation of these in soils of

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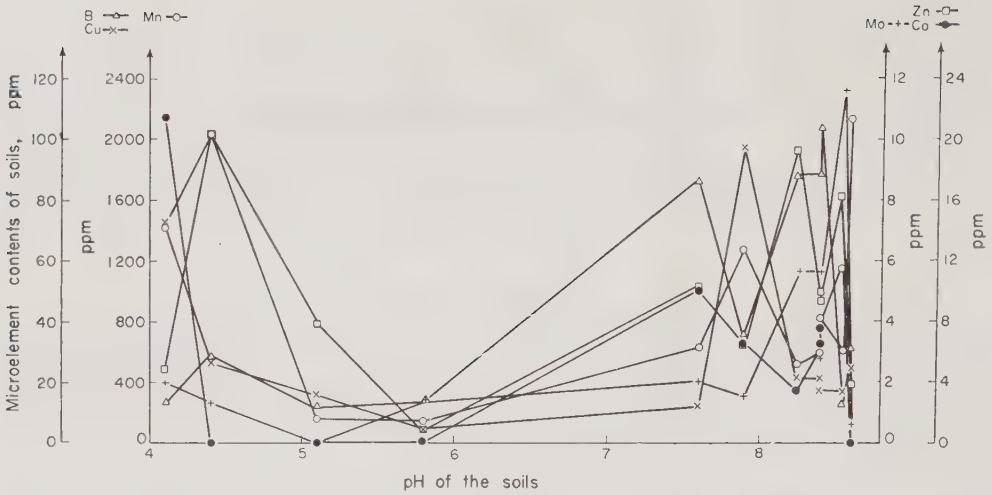

Fig. 1. Microelement contents of soils: ○ Manganese; △ Boron; × Copper; □ Zinc; + Molybdenum; ● Cobalt.

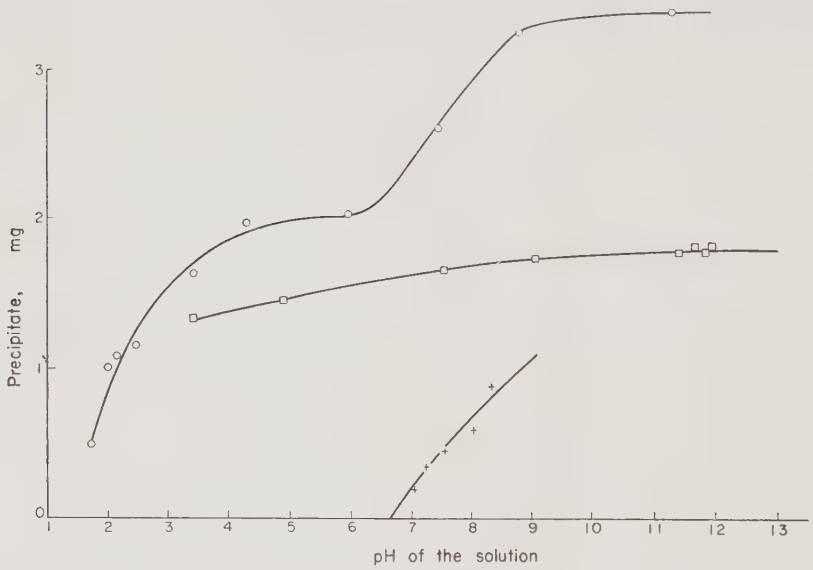

Fig. 2. Precipitation of microelements under different conditions of pH mark. ×, from solution containing microelements; □, from solution containing iron; ○, from solution containing microelements and iron.

pH values around 4·5 and 8·0. Fig. 2 gives the amounts of microelements and iron precipitated under different conditions of pH. Iron seems to influence the process of precipitation of microelements considerably.

The high microelement contents in soils around pH values 4·5 and 8·5 cannot be entirely accounted for as due to the soil parent materials. Preliminary experiments indicate that below pH 7·0, the microelements by themselves do not precipitate, whereas iron starts precipitating at pH 3·0. But when microelements and iron are

present together, a precipitate is formed at as low a pH as 1·8. Fig. 2 broadly indicates two pH regions of maximum precipitation at 4·5 and 8·5, respectively.

The geochemistry of a few elements only is well understood. The pH of the circulating waters is of the greatest importance in the geochemistry of manganese (Goldschmidt, 1954), the precipitation of which also depends on the aerobic and anaerobic conditions of the soils. Manganese precipitated as higher oxides can be leached only at pH values less than 4·0. In soils with pH of 7·0 or more, manganese is found to be strongly fixed in very insoluble higher oxides. At high oxidation potentials both iron and manganese precipitate as higher oxides. Copper, zinc and cobalt are sorbed on the residues from hydrolysis and especially to the hydroxides of iron and manganese. The same is true of molybdenum. Hence it is possible that iron and manganese influence the rest of the elements considerably during weathering processes and soil acidity is likely to control the microelement contents. Further work on the analysis of the precipitates obtained under different conditions of pH as well as a detailed study of the precipitation between pH value 4 and 5 is in progress.

Summary

An estimation of microelement contents, manganese, boron, copper, zinc, molybdenum and cobalt made in eleven typical samples of Indian soils indicated a concentration of these elements in soils with pH values around 4·5 and 8·5 respectively. Preliminary experiments conducted to study precipitation of microelements in solutions confirmed such a possibility. The results are discussed in relation to the sorption properties of the hydroxides of iron and manganese.

Acknowledgements—The authors gratefully thank Dr. B. Viswanath, Dr. K. V. S. Satyanarayana and Mr. Krishna Kumar for their help in the progress of the work. They also thank Dr. B. P. Pal, Director Indian Agricultural Research Institute, for the facilities offered to carry out this investigation.

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GEOCHEMICAL NOTES

Rhenium contents of rocks

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We have recently developed a neutron-activation method for the analysis of rhenium in rocks and some of the results obtained are reported here. Full details of the analytical procedure have been published elsewhere (Morris and Fifield, 1961). Radioactivation has special advantages as an analytical method from the points of view of sensitivity, specificity and the avoidance of contamination. Nevertheless, it is felt that the results quoted here should be taken as maximum values, since despite extensive precautions taken in the preparation of rock samples for analysis a complete freedom from contamination cannot be guaranteed.

In Table 1 are shown our results for rhenium in the standard granite G-1 and in the standard diabase W-1.

Table 2 records results for the rhenium content of gabbroid rocks from the Insch Mass,

Table 1. Rhenium analyses of the standard granite G–1 and the standard diabase W–1

G–1 (Re p.p.m.)	W–1 (Re p.p.m.)
0·00052	0·00070
0·00084	0·00059
0·00057	0·00083
0·00071	0·00056
0·00076	0·00084
0·00061	
av. 0·00067	av. 0·00071

Table 2. Rhenium content of some igneous rocks

	Rock	Re p.p.m.
3645	Syenogabbro, S. slope of Gallow Hill, Aberdeenshire	0·00036
3731	Syenite, S.W. slope of Gallow Hill, Aberdeenshire	0·00018
3815	Troctolite, 400 yds. W. of Barra Castle, Aberdeenshire	0·00031
3818	Hybridized dionite, S. of Druminor House, Chatt, Aberdeenshire	0·00016
5156	Albite-riebeckite-granite, Liruei	0·00112
5157	Biotite-granite, Liruei	0·00022
5159	Quartz-pyroxene-fayalite-porphyry, Liruei	0·00029
5160	Rhyolite, Liruei	0·00114
5169	Riebeckite-aegirine-granite, Liruei	0·00025
5799	Comendite, Liruei	0·00033

Aberdeenshire, Scotland, and of granitic rocks from Liruei, Nigeria. We are indebted to Dr. J. R. Butler for supplying us with samples of these rocks; the sample numbers listed are those of the Department of Geology, Imperial College, London,

Portions of "Specpure" silica (Johnson Matthey and Co.) were also analysed by our method and showed rhenium contents of 0·010 and 0·012 p.p.m. The samples had presumably been slightly contaminated in the production process and this illustrates the difficulty of obtaining reliable data for such a rare element as rhenium in rocks.

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pH of a natural hydrothermal solution

(*Received* 29 *April* 1961)

In comment on the geochemical note by A. J. Ellis (1960) in this journal it is desired to point out a necessary modification in calculating the pH of hydrothermal solutions.

The content of bicarbonate in samples taken at the surface from bore discharges is variable and cannot be used in conjunction with the carbon dioxide content of the whole discharge to calculate the pH of the underground water. Both boric and silicic acids, although weaker acids than carbonic acid, are in such high concentration that the presence of borate and silicate ions must be considered. The best samples of water are obtained from the weir boxes of twin tower silencers (Smith 1958, p. 363). This water is separated at atmospheric pressure from about 30 per cent of steam and most of the carbon dioxide is removed with the steam. When the sample is cold, the pH is high enough for the contents of borate and silicate ions to be appreciable. In the original water underground the higher concentration of carbon dioxide causes the replacement of borate and silicate ions by bicarbonate ion.

To illustrate this I have taken the average composition of the water from five bores at Wairakei, New Zealand, with water of the highest silica content. The discharge of the bore No. 31 of which the composition is given by Ellis is low in enthalpy from loss of steam underground by withdrawal in other bores. The pH calculated from the average composition given here should be closer to that of the original hydrothermal water.

The average composition of five samples of water separated at atmospheric pressure from bores 27, 46, 48, 55, 81 is—Cl: 63·5 m.p.m. (moles per million grams); HCO_3^-: 0·15 m.p.m.; total B as HBO_2: 2·85 m.p.m.; total Si as SiO_2: 9·44 m.p.m.; pH at 18°C: 8·55. The average enthalpy of the discharge was 465 B.t.u./lb (water fraction at atmos. pressure 0·702).

The apparent dissociation constant for boric acid at 18°C and ionic strength 0·065 was found to be $0{\cdot}69 \times 10^{-9}$ by interpolation from tables for sea-water given by Harvey (1955). The value of the constant for silicic acid (see below) was obtained from the value given for log K_A by Roller and Erwin (1940) at 30°C by using the formula of Pitzer (1937) with correction for ionic strength on the assumption that silicic acid is very similar to boric acid.

From the values for boric and silicic acids the contents of borate and silicate ions were found to be 0·57 m.p.m. and 0·38 m.p.m. respectively.

The content of sodium ions associated with the total of bicarbonate, borate and silicate ions is 1·10 m.p.m. and bicarbonate content can vary between this and 0·15 m.p.m. according to the content of carbon dioxide in solution.

The concentration of chloride ions and total boric and silicic acids in the underground water are obtained by use of the factor 0·702 (water fraction). The average content of carbon dioxide in the underground water was 5·8 m.p.m. (based on unpublished analyses by W. A. J. Mahon, Dominion Laboratory, who also analysed the waters). From the enthalpy of the discharge the temperature of the underground water is 250°C. The approximate apparent dissociation constants at 250°C are calculated from the values at 18°C for ionic strength 0·045 from the formula of Pitzer (1937) which was used by Ellis (1960) in his calculation of the pH at 230°C. The fractions of the total carbonic, boric and silicic acids present as anions can be calculated from the usual formula.

No appreciable amounts of other weak acids have been found, so that the sum of the contents of these three anions = 1·10 × 0·702 m.p.m. (see above). The four equations would give a cubic equation for the hydrogen ion concentration but as the contents of borate and silicate are low, the hydrogen ion concentration can easily be found by successive approximations. The pH of the underground water was found to be 5·75.

The composition of the underground water is—Cl:1580 p.p.m.; CO_2:301 p.p.m.; HCO_3^-:47 p.p.m.; HBO_2:87 p.p.m.; BO_2^-:0·3 p.p.m.; SiO_2:397 p.p.m.; $HSiO_3^-$:0·7 p.p.m.

The pH of a neutral solution at 250°C can be calculated from K_W at 25°C for a solution of 0·045 ionic strength ($1{\cdot}45 \times 10^{-14}$) and the formula of Harned and Owen (1950, p. 492). The pH is 5·65 as compared to 5·7 for pure water.

In the analysis of water samples from bore discharges it is not the actual content of bicarbonate that is important, but the content that could be present at the pH where boric and silicic acids just cease to be appreciably dissociated. So far this content has to be found by calculation of the content of borate and silicate at the pH of the sample. The calculated content of borate cannot be much in error. Much of the additional content of bicarbonate is due to the silicate ion content which is calculated from the dissociation constant, the pH and the content of silica which is assumed to be present entirely as silicic acid. Until now the determination of the pH of the samples has been made on the average about a day after collection. There was a possibility that in this time there had been appreciable polymerisation of silicic acid. It seemed desirable to check this point and to make sure that the dissociation constant used was, in fact, applicable to these samples.

A stock of water was prepared from A.R. chemicals so that the composition was the same as the average composition of water samples given above, except that boric acid and bicarbonate were omitted. Samples of this water were heated to 250°C in a stainless steel bomb, cooled rapidly and allowed to stand about a day. The average change in pH of the samples on standing was 0·1 unit to the acid side, the wrong direction for polymerisation.

50 ml of the sample was adjusted to pH 8·5 and titrated with 0·02 N hydrochloric acid. The change in pH was followed by a pH meter and glass electrode. By comparison of the titration curve with that for synthetic water with no silica, the dissociation constant was found to be approximately $0{\cdot}17 \times 10^{-9}$ instead of the value used above, $0{\cdot}12 \times 10^{-9}$.

A similar test was made with synthetic water of ionic strength 0·045, but the samples were titrated immediately after cooling from 250°C. The dissociation constant was $0{\cdot}16 \times 10^{-9}$ instead of the value $0{\cdot}11 \times 10^{-9}$ used to calculate the constant at 250°C.

These check tests are not to be taken as new determinations of the dissociation constant of silicic acid, but they indicate that the values used above cannot be greatly in error.

It appears that the underground chloride water at Wairakei is very nearly neutral.

The conclusion of A. J. Ellis that these hydrothermal solutions should not be called "alkaline" still holds, for there can be no sharp distinction between waters so near the neutral point especially as the calculated values of the dissociation constants at 250°C are so uncertain. The true pH of hydrothermal solutions cannot be known till there are determinations of the dissociation constant of carbonic acid at high temperatures. Changes in the value taken for the constant for boric acid may not have much effect, but the calculated pH will be affected by more accurate values for the dissociation constant of silicic acid at both high and low temperatures.

It also appears (Harned and Owen, 1950, p. 580) that the second dissociation constant of sulphuric acid falls quickly with rise of temperature, so that at 250°C SO_4^{2} ions may be replaced by HSO_4^- ions. At Wairakei the sulphate content is low (0·26 m.p.m.) but even so the effect would bring the pH to 5·85 and at Waiotapu (another New Zealand thermal area with waters essentially similar to those at Wairakei but with sulphate three times as high) the pH would be shifted appreciably to the alkaline side.

On the other hand the pH of underground hydrothermal solutions cannot be far on the alkaline side of neutral. Hot spring waters of high chloride content have been found in which a high sulphate content seems to be a constituent of the underground water and not just due to surface oxidation. An example is the water of the Rotokawa thermal area near Wairakei with chloride about 500 p.p.m. and sulphate 1,000 p.p.m. On cooling the pH of such waters will go to the acid side owing to the reaction $HSO_4^- = H^+ + SO_4^{2-}$ as this will outweigh the effect of the loss of carbon dioxide. This may explain the acidity of chloride-sulphate springs. (At Rotokawa the pH is about 2·5.)

It is not possible to make even an approximate calculation of the second dissociation constant of sulphuric acid at 250°C. Hence determinations of the dissociation constants at high temperatures for a number of acids are required before it can be said whether hydrothermal solutions are on the acid or alkaline side of neutral.

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BOOK REVIEWS

ANDRE VOISIN. **Soil, Grass and Cancer.** Philosophical Library, New York, 1959. 302 pp.

THIS book, written by an experienced agriculturalist who is extremely widely read and well informed, is highly suggestive and valuable. His fundamental thesis is that (1) the soil makes the grass (fodder), (2) the grass makes the animal, (3) the soil makes the man. "Animals and men," he says, "are the biochemical photograph of the soil".

The author makes a strong case for the influence of the soil on a large number of human diseases among which are some such as endemic goitre that are well recognized and established. Diseases of animals caused by mineral lacks or inbalances, the world over, are reviewed; many of these observations of course have a firm foundation. In the course of the sixty-six chapters—rather a discursive array—the author discusses the importance of boron, iodine, phosphate, calcium, sulfate, potassium, sodium, iron, copper, molybdenum, magnesium, manganese, zinc, and cobalt. His sophistication is shown by his realization that a traditional chemical analysis of a soil or water or foodstuff needs supplementation by biological experiments, partly because in the trace element field, for example, chelation may be an important factor. He cites evidence to prove and emphasizes the fact that mineral deficiencies or imbalances in the soil may result in altered metabolism in the "grass" so that the production of specific amino acids, vitamins (vitamin A conspicuously), and possibly other nutritionally important items is decreased. Accordingly he emphasizes that when 'milk' or some vegetable product is used in a nutritional experiment, the results may be meaningless unless the character of the soil from which the product was derived is specified. He emphasizes the fact that we remove with crops all of the nutritionally important elements from the soil but we tend to replace not more than four or possibly seven in fertilizers. He advocates the judicious and intelligent use of all types of fertilizers.

Having become convinced that many human ills can be traced to the soil, it is but natural that the author inquires into the problem of cancer. The most definite evidence presented on this subject has to do with cancer statistics in Wales and in Holland as they are related to the types of soil and the drinking water used. One would be rash indeed to hold the opinion after reading Voisin's book that soil has nothing to do with cancer.

While this book may give pleasure and comfort to certain faddists, who will select from it what they most like, the author deserves commendation for his attempt to be objective and at the same time stimulative. The contents of the volume should not be swallowed whole. The author seems inclined, for example, to minimize the genetic aspects of the problem. However, the various ideas suggested merit digestion and critical consideration. The book is an important one.

ROGER J. WILLIAMS

Descriptive Palaeoclimatology (Edited by A. E. M. NAIRN). Interscience, New York. 1961. price 80s.

THIS book is a symposium of fourteen chapters contributed by experts from several countries. The greater part is concerned with a critical presentation of the various lines of evidence used in

constructing a picture of the earth's climatic history. Most of the evidence is drawn from physiographical studies of desert and glacial terrain, the interpretation of the lithology of rocks such as evaporites and Red Beds, and the correlation between fossils and climate. The application of geophysics is discussed in sections on palaeomagnetism (Chap. 7) and on the fundamentals of climate (Chap. 2).

Geochemical studies relevant to Palaeoclimatology are described in sections dealing with the measurement of marine palaeotemperatures by the oxygen isotope method (Chap. 7), theoretical and experimental work on the stability relations of the evaporite minerals (Chap. 4), and the chemistry of the iron-oxide minerals of Red Beds (Chap. 5). These topics are, of necessity, dealt with only briefly in a general work of this kind, but in each of these three chapters it is made clear that the geochemical data are of fundamental importance to the science of Palaeoclimatology, and that there is a need for much more geochemical work in this field.

G. M. Brown

E. L. Krinov: **Principles of Meteoritics.** Translated by Irene Vidziunas and edited by Harrison Brown. Pergamon Press, London. 1960. xi + 535 pp., 154 figs. 7 plates. 70s. net.

This English translation of Krinov's *Principles of Meteoritics* does not do justice to the original. The translation is sound, but the attempt to bring the edition up to date has failed, partly because it is not possible to distinguish the new matter from the old (which it often corrects or contradicts). The numerous tables are set out in an unnecessarily clumsy fashion; a number of new references have been added to the list of literature at the end of the book, but the references in the text to this list have often remained uncorrected. The half-tone figures (themselves one of the weaker features of Krinov's, as of many Russian books) are thoroughly unsatisfactory in a book offered at so high a price; some loss in reproduction is inevitable if the original blocks were not available but, for example, the deterioration in Figs. 30 and 42 is very grave. The attempt to produce a Roman alphabet version of Fig. 52 (one of the most useful in the original book, showing the place of fall of every Russian meteorite) has been abandoned half-way through and the incomplete map printed. A most disappointing edition of a good book.

The eight chapters are: Meteoritics as a branch of science; Motion and fall of meteorites; Morphology of meteorites; Chemistry; Mineralogy and Petrography; Physical properties; Tektites and silica glass; Origin of meteorites. Three appendices give: A catalogue of meteorites of the U.S.S.R.; Lists of siderites observed to fall, of stony-irons, of brecciated meteorites and, of carbonaceous chondrites and of achondrites; A classification of the surface structure of the fusion crust of meteorites.

M. H. H.

Geochimica et Cosmochimica Acta, 1961, Vol. 25, p. 238. Pergamon Press Ltd. Printed in Northern Ireland

NOTICE

International Mineralogical Association

PRELIMINARY ANNOUNCEMENT, 1962 MEETING, WASHINGTON, D.C.

SCHEDULE

Northern Field Trip (New York-Washington)		April 14–16, 1962
Washington Meeting		April 17–20, 1962
Commission meeting	April 17	
Scientific sessions	April 18–20	at U.S. National Museum
Reception welcome	April 17	at Marriott Motor Hotel, 5 P.M.
Dinner	April 19	at Marriott Motor Hotel, 7 P.M.
Southern Field Trip (Washington-Virginia-Washington)		April 20–22, 1962

PRELIMINARY plans for the 1962 meeting of the International Mineralogical Association in Washington, D.C. have been formulated as outlined in the schedule above. April is one of the busiest months of the year in Washington as far as visitors are concerned and we have been fortunate in being able to reserve accommodation and other facilities at the Marriott Motor Hotel, on the Potomac River in Virginia. The Local Committee is planning to provide accommodations for the majority of visitors from outside the country through the hospitality of scientists residing in the Washington area. Various activities for accompanying family members are being planned under the direction of Kathleen Roedder. The Mineralogical Society of America has applied for financial assistance toward travel for participants, field trips, and publication expenses for the meeting, and as soon as it is known to what extent these funds may be available, a more definite notice will be distributed with information on the cost and other details.

The program for the scientific sessions and the agenda for the commission meetings are still in the process of formulation and will be announced later.

FIELD TRIPS

Northern Field Trip — Leader: PAUL F. KERR — April 14–16, 1962

April 14: New York City. Visits to the American Museum of Natural History, Columbia University Department of Geology, and Lamont Geological Observatory.

April 15: Paterson, New Jersey (zeolites) and Franklin Furnace, New Jersey (zinc)

April 16: Cornwall, Pennsylvania (sphalerite, magnetite, etc.)

Total cost will not exceed $50.00 including transportation, lodging, and food.

Southern Field Trip — Leader: Richard V. Dietrich — April 20–22, 1962

Leave Washington early evening of April 20 for Amelia Court House, Virginia, arriving later in the evening.

April 21: Amelia Court House (pegmatite), Willis Mountain (kyanite), and Roseland (rutile)

April 22: Miscellaneous Virginia localities (unakite, clay, bauxite, manganese) Luray Caverns.

Total cost will not exceed $50.00 including transportation, lodging, and food.

D. JEROME FISHER, President
Rosenwald Hall
University of Chicago
Chicago 37, Illinois

ALVIN VAN VALKENBURG
IMA Local Committee Chairman
National Bureau of Standards
Washington 25, D.C.

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I. GENERAL

1. Papers on *geochemistry* should be submitted to the appropriate Executive Editor—Prof. L. R. WAGER for papers from the United Kingdom and British Commonwealth and for papers in English from Europe; PROF. C. W. CORRENS for papers in German or French; Prof. J. A. S. ADAMS for papers from the American continents. Papers submitted for publication will naturally be judged from the standpoint of scientific originality and novelty. Technical details of apparatus used in scientific investigation can, however, be presented in brief notes. Critical comments or preliminary results requiring early publication should be submitted as letters to the editors. Where possible, letters should be confined to 500 words. The preparation of progress reports and review articles will be invited by the editors from time to time. The journal appears as independent and complete numbers, which are combined into volumes of about 300 pages.

2. Only papers which have not been previously published can be accepted. Authors must agree not to publish elsewhere a paper submitted to and accepted by *Geochimica et Cosmochimica Acta*.

3. Fifty reprints of each paper are provided free. Additional copies can be purchased if ordered at the time the first proofs are returned. A reprint order form will accompany first proofs.

II. SCRIPT REQUIREMENTS

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2. The script should be typed (not a carbon copy). The text must be ready for printing and should be carefully checked for errors. Authors will receive proofs for correction. The original script plus two copies will assist in expediting publication.

3. Illustrations should accompany the script mounted on separate sheets. Line diagrams that require to be redrawn should include all relevant details. Half-tone illustrations should be restricted to the minimum necessary. Photographs should be enlarged sufficiently to permit their clear reproduction and if words or numbers appear on them, two copies should be sent, one clearly printed and the other without inscription. All illustrations should be provided with descriptive legends, which should be given on a separate sheet. Any lettering on diagrams—other than Greek letters, symbols, etc.—should be stencilled and should be sufficiently large and bold to permit reproduction when the diagram has been reduced to a size suitable for inclusion in the journal.

4. References in the text should be given by quoting the author's name and year of publication, i.e. AHRENS (1952). *Full references should be listed at the end of each paper, in alphabetical order, in the following manner*

AHRENS, L. H. (1952). The use of ionization potentials—I. Ionic radii of the elements. *Geochim. et Cosmochim. Acta* **2**, 155–169.

and should include the full title of the article, standard abbreviated title of the journal, year, volume number and inclusive page numbers.

5. The text of articles submitted should be concise and in a readily understandable style. The technical description of the methods used should only be given in detail when such methods are new. The essential contents of each paper should be briefly recapitulated in an abstract in English. Such an abstract may, however, be submitted by the author in the language of the original typescript for translation into English by the editorial staff.

6. To conserve space, authors are requested to mark less important portions of the paper (such as description of methods, record of experimental results, etc.) for printing in smaller type.

7. Indices of refraction should be denoted by the symbols α, β, γ, ω, ε, n, and vibration directions by X, Y, Z, O and E.

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